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ENVIRO
TIPS
Technical Information for Problem Spills

ETHYLENE OXIDE

May 1985

Canada

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ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals provide detailed information on chemical substances. This information is intended to assist the reader in designing countermeasures for spills and to assess their impact on the environment. The report has been reviewed by the Technical Services Branch, Environmental Protection Service, and approved for publication. Approval does not signify that the contents reflect the views and policies of the Environmental Protection Service. Mention of trade names or commercial products does not constitute endorsement for use.

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ETHYLENE OXIDE

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

Technical Services Branch
Environmental Protection Programs Directorate
Environmental Protection Service
Ottawa, Ontario

May 1985

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FOREWORD

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals were initiated in 1981 to provide comprehensive information on chemicals that are spilled frequently in Canada. The manuals are intended to be used by spill specialists for designing countermeasures for spills and to assess their effects on the environment. The major focus of EnviroTIPS manuals is environmental. The manuals are not intended to be used by first-response personnel because of the length and technical content; a number of manuals intended for first-response use are available. The information presented in this manual was largely obtained from literature review. Efforts were made, both in compilation and in review, to ensure that the information is as correct as possible. Publication of these data does not signify that they are recommended by the Government of Canada, nor by any other group.

ACKNOWLEDGEMENTS

The final version of this manual was prepared by the staff of the Environmental Protection Service who wrote extensive revisions to the text, drafted illustrations and incorporated all comments and additions.

The level of detail present was made possible by the many individuals, organizations and associations who provided technical data and comments throughout the compilation and subsequent review of and input to this manual. The draft of this manual was prepared under contract to Environment Canada by M.M. Dillon Consulting Engineers and Planners, Concord Scientific Corporation, and Waterloo Engineering Limited.

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1 SUMMARY

ETHYLENE OXIDE (CH_2OCH_2)

Colourless gas with a sweet, ether-like odour.

SYNONYMS

Dimethyl Oxide, 1,2-Epoxyethane, Epoxyethane, ETO, Oxacyclopropane, Oxane, Oxidoethane, Oxiran, Oxirane, Anprolene, Dihydro-oxirene, E.O., Dimethylene Oxide

IDENTIFICATION NUMBERS

UN. No. 1040, 1041 (for mixtures containing not more than 10 percent carbon dioxide), 1952 (for mixtures containing not more than 17 percent ethylene oxide in carbon dioxide), CAS No. 75-21-8; OHM-TADS No. 7216724; STCC No. 4906610

GRADES & PURITIES

Commercial grade, >99.9 percent

IMMEDIATE CONCERNS

Fire: Flammable. Vapours are detonatable. Fires are difficult to control.

Human Health: Highly toxic by ingestion and moderately toxic by inhalation. Suspected carcinogen.

Environment: Harmful to aquatic life.

PHYSICAL PROPERTY DATA

Shipping state: liquid (under pressure)
State (15°C, 1 atm): gas
Boiling Point: 10.4°C
Freezing Point: -112.5°C
Flammability: flammable
Flash Point: <-18°C (CC)
Vapour Pressure: 101 kPa (10°C)
Vapour Density: 1.49
Density: 0.8969 (liquid, 0°C)
Solubility (in water): completely soluble
Behaviour (in water): liquid floats and mixes
Behaviour (in air): vapour forms explosive mixtures with air
Odour Threshold Range: 250 to 7000 ppm

ENVIRONMENTAL CONCERNS

Ethylene oxide is toxic to fish at concentrations as low as 90 mg/L. It affects germination of seeds and shows mutagenic effects in plants.

HUMAN HEALTH

TLV®: 1 ppm (2 mg/m^3)

IDLH: 800 ppm

Exposure Effects

Inhalation: Vapour is irritating to the eyes, upper respiratory tract, and lungs. Causes headache, dizziness, drowsiness, coughing, nausea, difficult breathing, central nervous system depression and pulmonary edema.

Contact: Contact with skin or eyes causes irritation and burns. May cause eczema-like skin sensitization, blistering, frostbite to skin and possibly dermatitis.

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning "FLAMMABLE & POISON". Call fire department and notify manufacturer. Eliminate sources of ignition including traffic and equipment. Stop the flow and contain spill, if safe to do so. Avoid contact with liquid and vapour; stay upwind of release. Keep contaminated water from entering sewers or watercourses.

Fire Control

Do not extinguish fire unless release can be stopped. In case of fire, do not reduce source pressure. Cool fire-exposed containers with water. Use alcohol foam, dry chemical and carbon dioxide to extinguish. Water spray will not put out fire, until the spill is heavily diluted. Stay clear of tank ends. Reignition or explosion can occur after fire is extinguished.

COUNTERMEASURES

Emergency Control Procedures in/on

Soil: Construct barriers to contain spill.

Water: Contain by damming, water diversion or natural barriers. If possible, treat water in situ or remove for treatment.

Air: Use water spray to knock down and disperse flammable vapour. Control runoff for later treatment and/or disposal.

NAS HAZARD RATING

Category	Rating
Fire	4
Health	
Vapour Irritant	3
Liquid or Solid Irritant	3
Poison	2
Water Pollution	
Human Toxicity	3
Aquatic Toxicity	2
Aesthetic Effect	1
Reactivity	
Other Chemicals	3
Water	1
Self-reaction	4

NFPA
HAZARD
CLASSIFICATION

2 PHYSICAL AND CHEMICAL DATA

Physical State Properties

Appearance	Clear colourless gas at 20°C. At colder temperatures, it condenses to a colourless liquid (Dow MSDS 1980)
Usual shipping state	Liquid: under pressure (Dow ERIS 1981)
Physical state at 15°C, 1 atm	Gas
Freezing point	-112.5°C (Kirk-Othmer 1980)
Boiling point	10.4°C (Kirk-Othmer 1980)
Vapour pressure	101 kPa (10°C) (CRC 1980)

Densities

Density (gas)	Liquid: 0.8969 g/mL (0°C) (Kirk-Othmer 1980) Gas: 1.795 kg/m^3 (20°C) (Matheson 1974)
Specific gravity	0.8824 (liquid, 10°/10°C) (CRC 1980)
Vapour density	1.49 (Celanese PB 1978)

Fire Properties

Flammability	Flammable liquid or gas depending on temperature (NFPA 1978)
Flash point	<-18°C (CC) (NFPA 1978) -17.7°C (Tag open cup) (Bridge 1980) 60°C (0.3 percent (w/w) solution in water) (Ullmann 1975) 32°C (2.5 percent solution in water) (Kirk-Othmer 1980) -2°C (5 percent solution in water) (Ullmann 1975) -6.5°C (12 percent solution in water) (Ullmann 1975)
Autoignition temperature	429°C (NFPA 1978)
Burning rate	3.5 mm/min (CHRIS 1978)
Upper flammability limit	100 percent (v/v) (NFPA 1978)
Lower flammability limit	3.0 percent (v/v) (Kirk-Othmer 1980)
Heat of combustion	1306 kJ/mole (25°C) (Kirk-Othmer 1980)
Combustion products	Carbon dioxide and water (CRC 1980)
Flashback potential	Vapour may travel considerable distance to source of ignition and flash back (NFPA 1978)

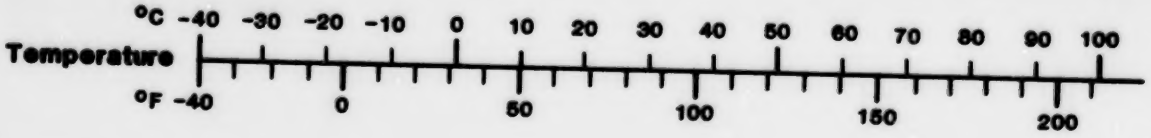
Explosiveness	Vapour forms explosive mixtures with air over wide range (NFPA 1978) Explosive potential is 0.75 compared to TNT (CCPA 1983)
Behaviour in a fire	Ethylene oxide/water solutions will continue to burn until diluted with 22 volumes water to 1 volume ethylene oxide (NFPA 1978). Can burn in very low oxygen atmospheres
Electrical ignition hazard	May be ignited by static discharge
Other Properties	
Molecular weight of pure substance	44.05 (CRC 1980)
Refractive index	1.3597 (liquid at 7°C) (CRC 1980)
Viscosity	9.45×10^{-3} mPa·s (25°C, gas), 0.254 mPa·s (10°C, liquid) (Matheson 1974)
Liquid interfacial tension with air	24.3 mN/m (20°C) (CRC 1980)
Hygroscopicity	Slight (Celanese PB 1978)
Latent heat of fusion	5.15 kJ/mole (at melting point) (CRC 1980)
Latent heat of sublimation	24.9 kJ/mole (25°C) (Lange's Handbook 1979)
Latent heat of vaporization	28.5 kJ/g mole (at boiling point) (CRC 1980)
Heat of polymerization	-92.1 kJ/mole (Ullmann 1975)
Heat of formation	-52.63 kJ/mole (25°C) (JANAF 1971)
Entropy	242.4 J/(mole·K) (25°C) (Kirk-Othmer 1980)
Ionization potential	10.56 eV (Krassig 1974)
Heat of solution	-6.25 kJ/mole (CHRIS 1978)
Electrical conductivity	2.1×10^{-8} ohm^{-1} m^{-1} (Ullmann 1975)
Dielectric constant	13.71 (liquid at 0°C) (Kirk-Othmer 1980) 1.61 (gas at 15°C) (Ullmann 1975)
Dipole moment	1.90 D (Kirk-Othmer 1980)
Heat capacity	
constant pressure (C_p)	88.46 J/(mole·°C) (liquid at 20°C), 48.28 J/(mole·°C) (gas at 25°C) (Kirk-Othmer 1980)
constant volume (C_v)	39.6 J/(mole·°C) (gas at 27°C) (CRC 1980; CHRIS 1978)
Critical pressure	7194 kPa (CRC 1980)
Critical temperature	195.8°C (CRC 1980)
Coefficient of thermal expansion	1.61×10^{-3}/°C (20°C) (Kirk-Othmer 1980)
Thermal conductivity	0.012 W/(m·K) (gas at 27°C) (Kirk-Othmer 1980)

	0.039 W/(m·K) (liquid at 20°C) (Matheson 1980)
Log_{10} octanol/water partition coefficient	-0.30 (Hansch and Leo 1979)
Solubility	
In water	Completely soluble (Dow MSDS 1980) 195 mL/mL (20°C) (Kirk-Othmer 1980)
In other common materials	Miscible with alcohol, ether and most organic solvents (Celanese PB 1978) Soluble in acetone, benzene, carbon tetrachloride and methanol (Ullmann 1975)
Vapour Weight to Volume Conversion Factor	
	1 ppm = 1.829 mg/m^3 (20°C) (1 mg/m^3 = 0.55 ppm) (Verschueren 1984)

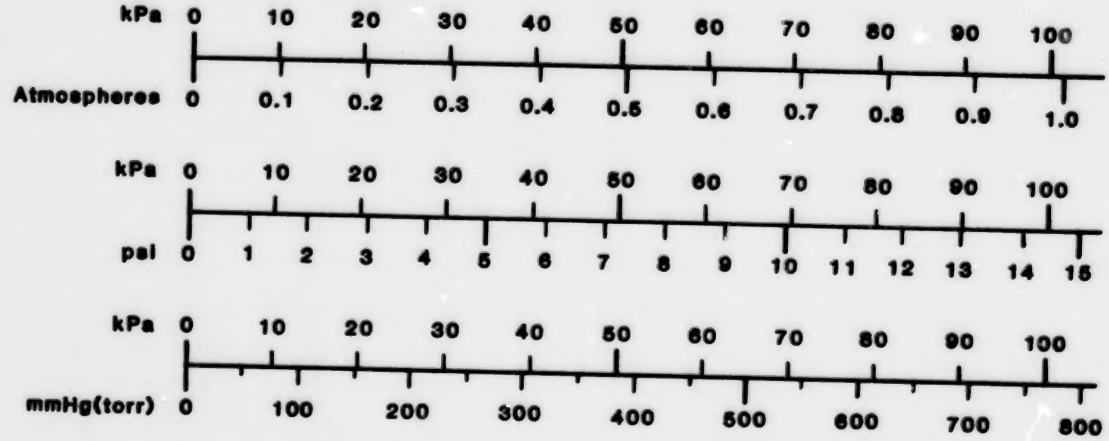
TABLE 1

ETHYLENE OXIDE

CONVERSION NOMOGRAMS



Pressure 1 kPa = 1 000 Pa



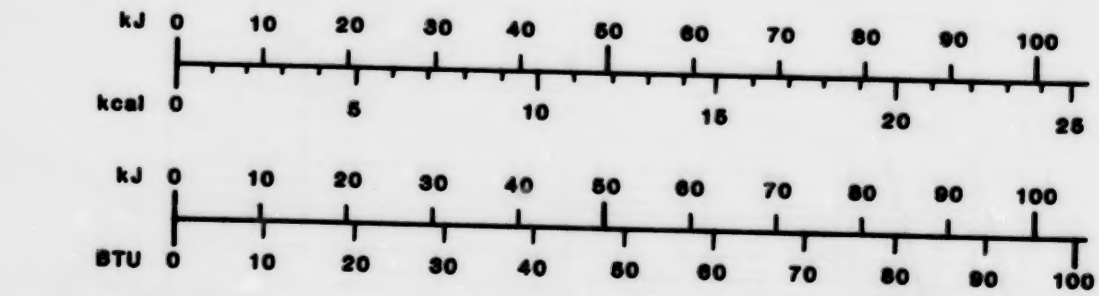
Viscosity

Dynamic 1 Pa·s = 1 000 centipoise (cP)

Kinematic 1 m^2/s = 1 000 000 centistokes (cSt)

Concentration (in water)
1 ppm ≅ 1 mg/L

Energy (heat) 1 kJ = 1 000 J



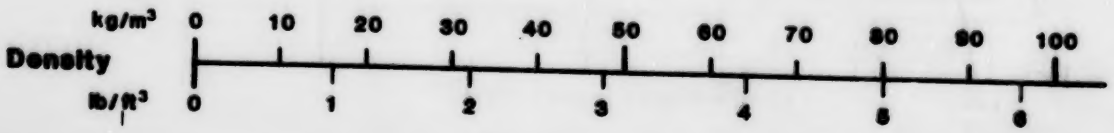


FIGURE 1

ETHYLENE OXIDE

VAPOUR PRESSURE VS TEMPERATURE

Reference: Chem:Eng. 1976

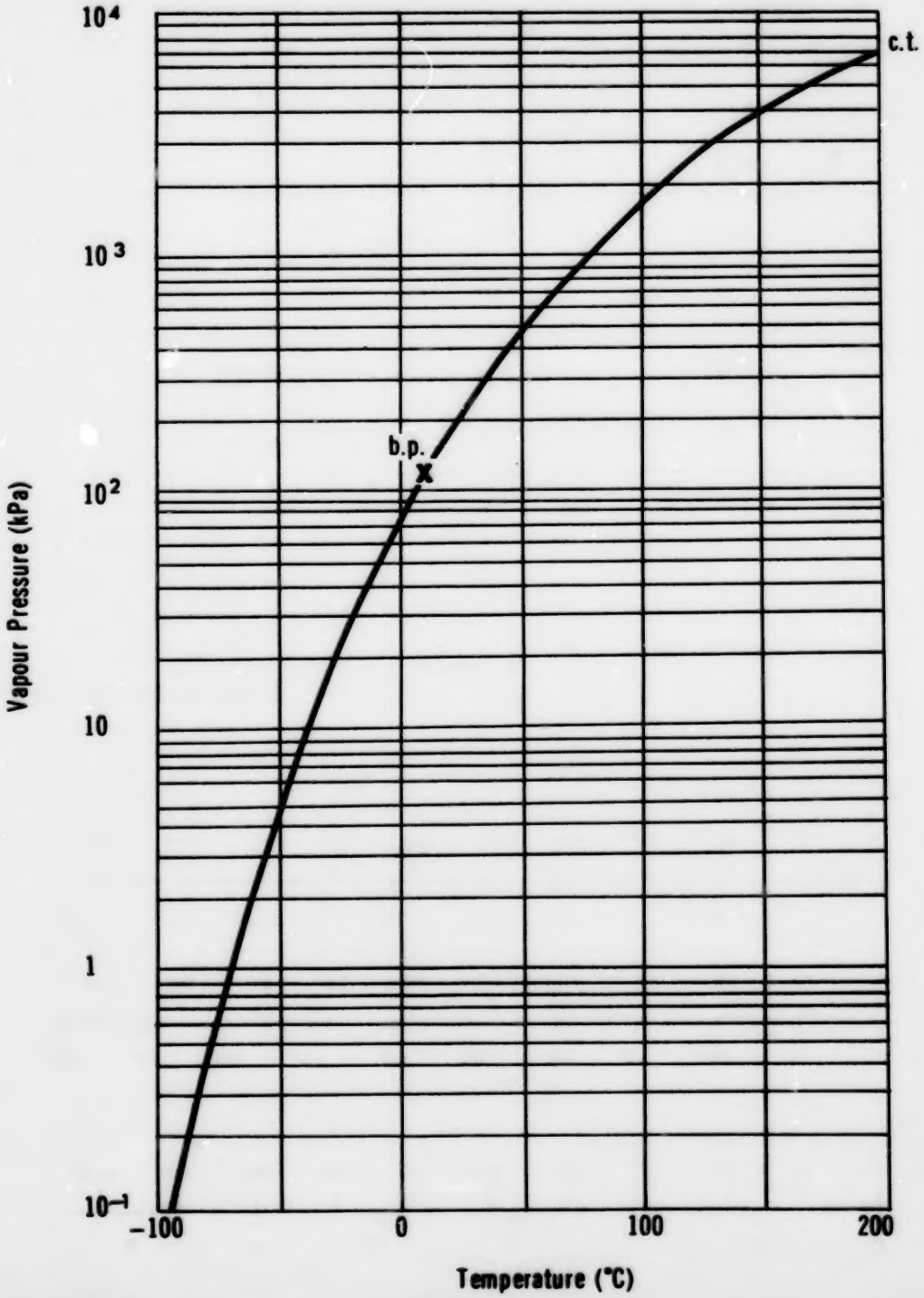


FIGURE 2

ETHYLENE OXIDE

PHASE DIAGRAM OF THE ETO-H_2O SYSTEM

Reference: KIRK-OTHMER 1980

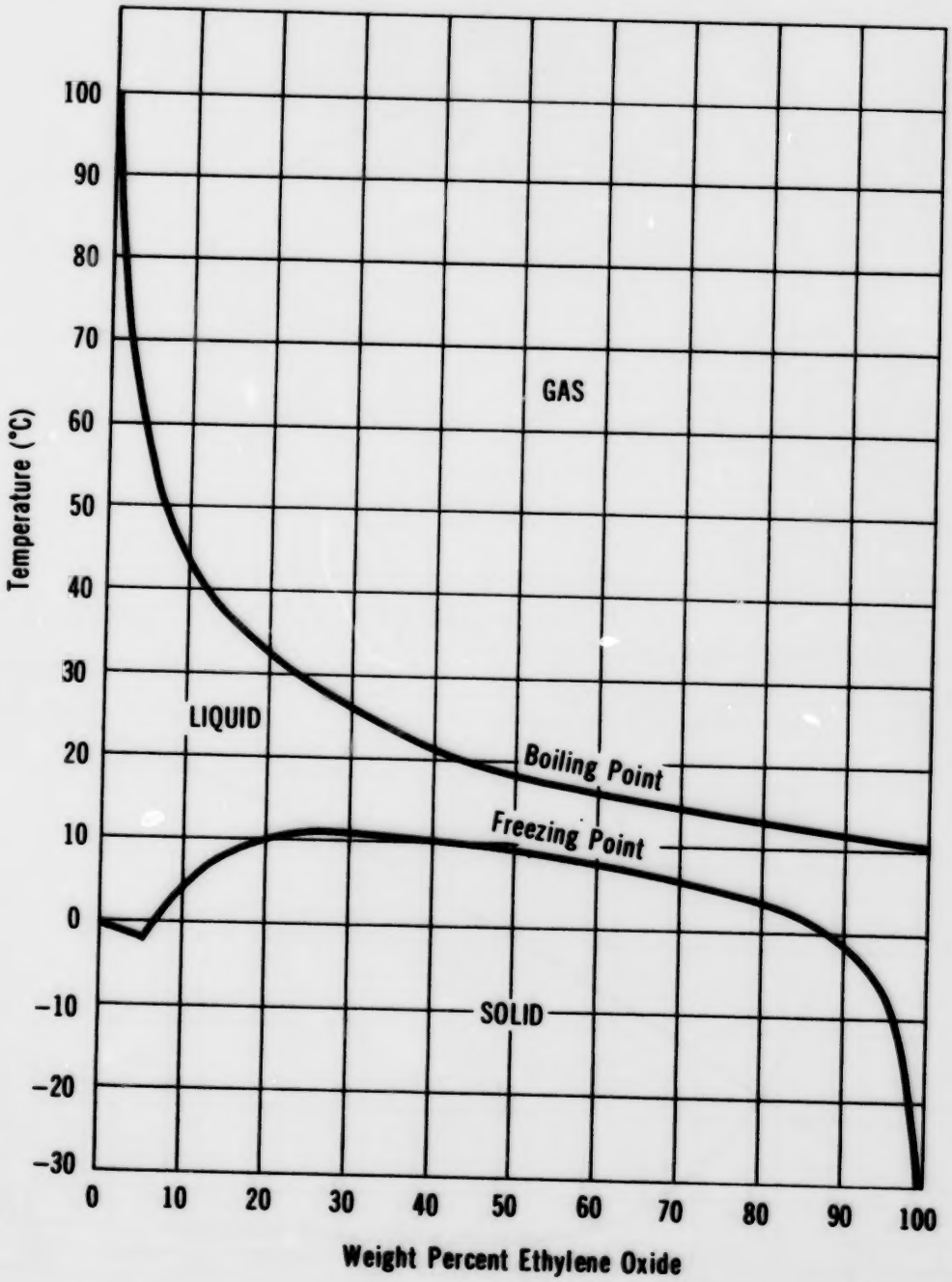


FIGURE 3

ETHYLENE OXIDE

LIQUID DENSITY VS TEMPERATURE

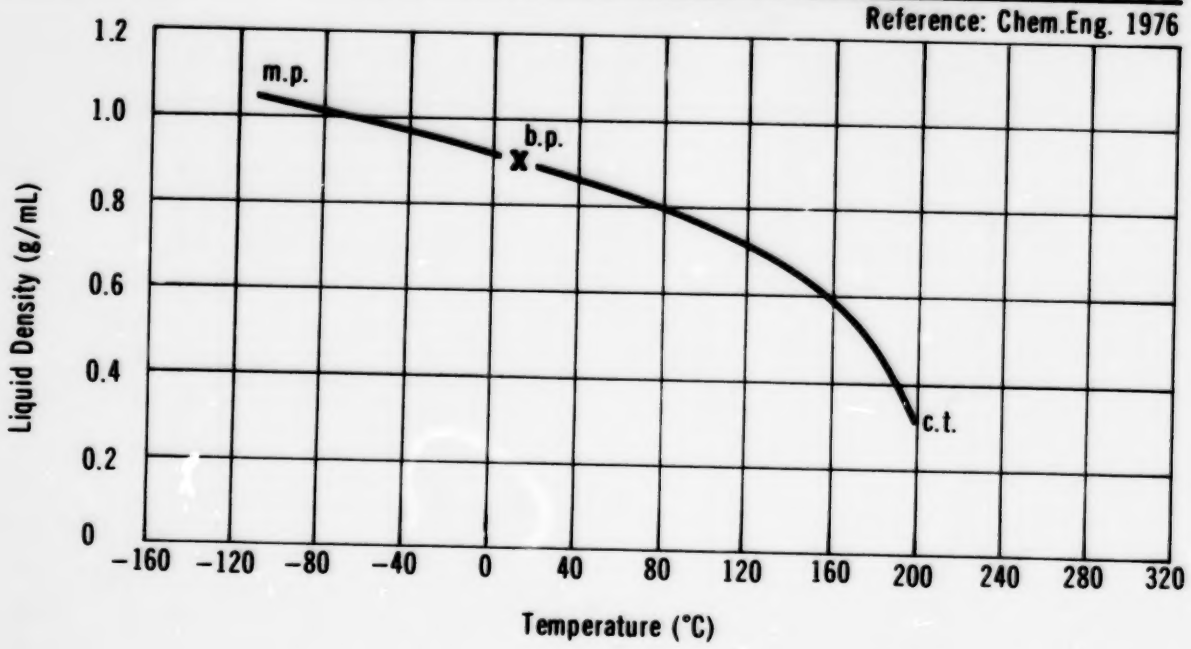


FIGURE 4

ETHYLENE OXIDE

VAPOUR VISCOSITY VS TEMPERATURE

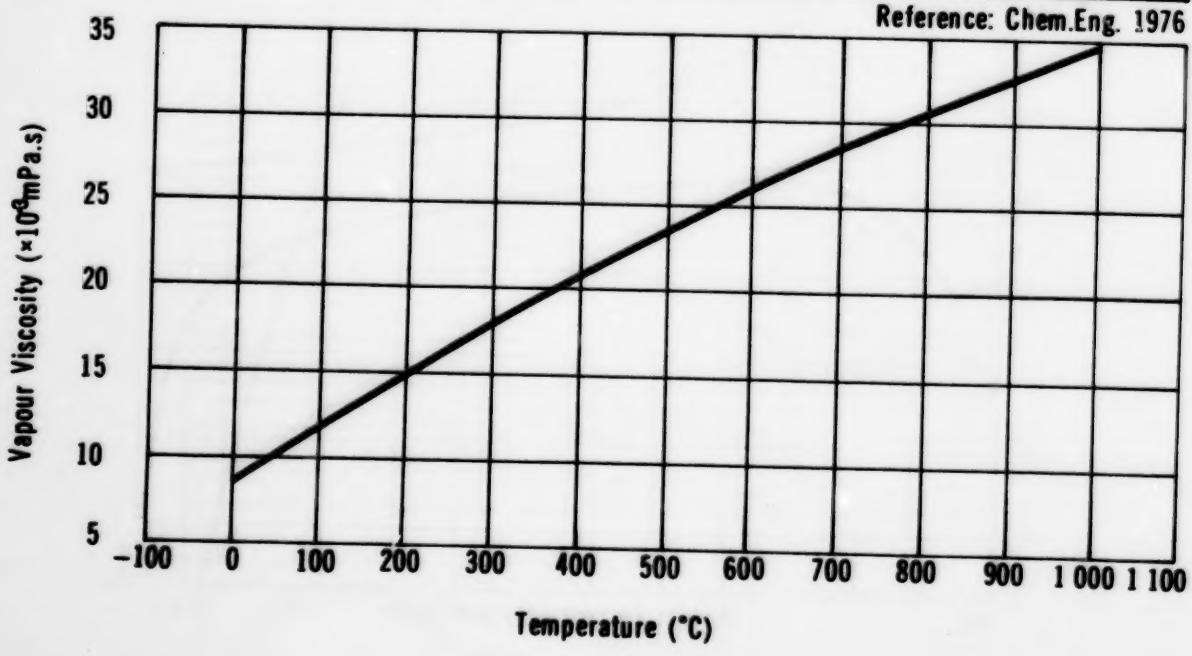


FIGURE 5

ETHYLENE OXIDE

LIQUID VISCOSITY VS TEMPERATURE

Reference: Chem.Eng. 1976

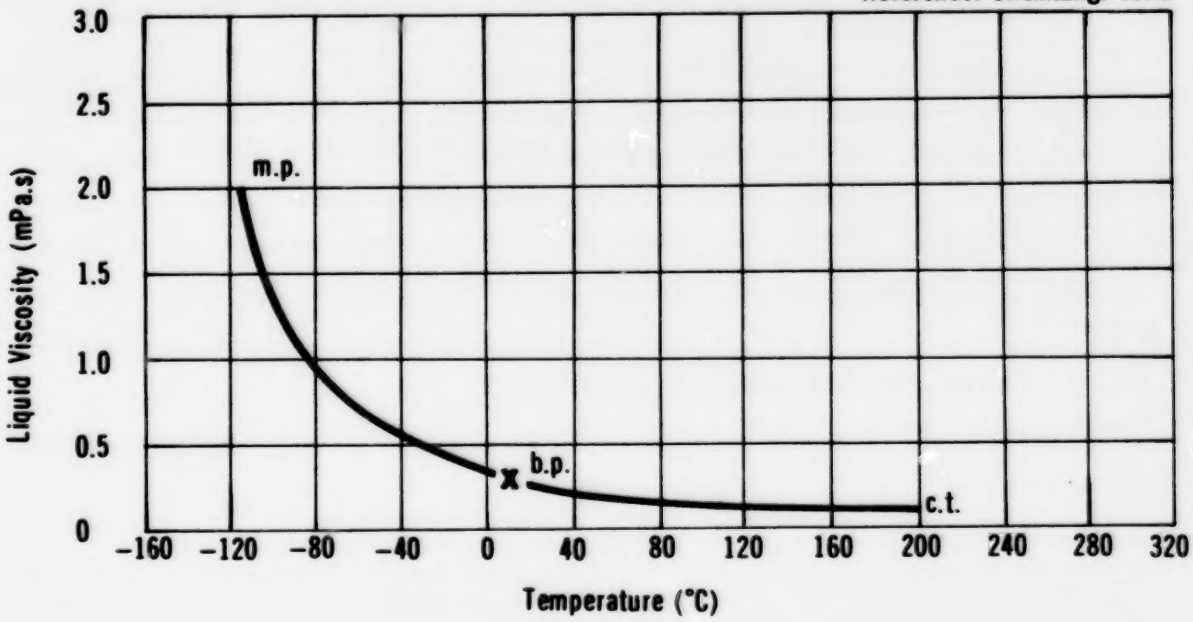
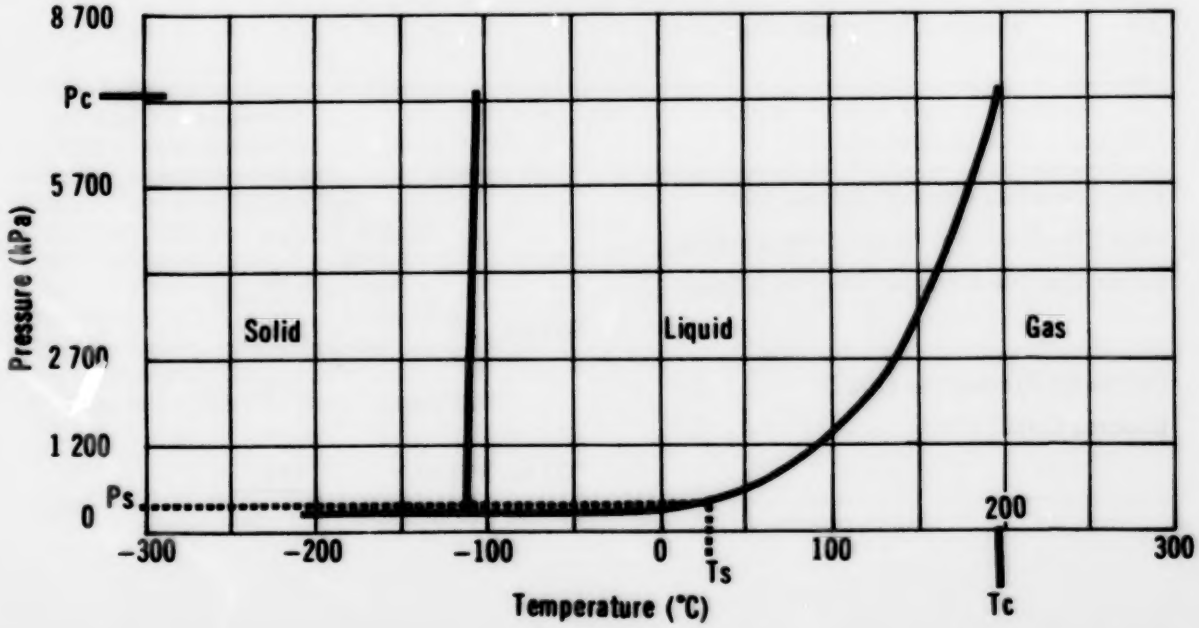


FIGURE 6

ETHYLENE OXIDE

PHASE DIAGRAM



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities (Celanese PB 1978; Kirk-Othmer 1980)

Ethylene oxide is commonly sold in a commercial grade with a minimum purity of 99.9 percent. Impurities may be specified: e.g., acid, 0.002 percent max. (as acetic acid); aldehydes, 0.003 percent max. (as acetaldehyde); water, 0.03 percent max.; and residue, 0.005 g/100 mL max. As a sterilant, ethylene oxide is often mixed with carbon dioxide as 12/88 (v/v - ETO/CO_2) and 10/90. It is also mixed with dichlorofluoromethane in similar proportions. These mixtures are not often shipped nor are they taken as "grades".

3.2 Domestic Manufacturers (Corpus 1983; CCPA 1981)

These are corporate headquarters' addresses and are not intended as spill response contacts:

Dow Chemical Canada Inc.
Box 1012, Modeland Road
Sarnia, Ontario
N7T 7K7
(519) 339-3131

Union Carbide Canada Ltd.
123 Eglinton Avenue East
Toronto, Ontario
M4P 1J3
(416) 488-1444

3.3 Major Transportation Routes

Current Canadian production of ethylene oxide is located in Montreal, Quebec, in Fort Saskatchewan, Alberta, and in Sarnia, Ontario. The product is commonly shipped by railway tank car across Canada.

3.4 Production Levels (Corpus 1983)

Company, Plant Location		Nameplate Capacity kilotonnes/yr (1982)
Dow Chemical Canada, Sarnia, Ont.		62.5
Dow Chemical, Ft. Saskatchewan, Alta.		145
Union Carbide Canada, Montreal, Que.		75
	TOTAL	282.5
Domestic Production (1982)		169
Imports (1982)		-
	TOTAL SUPPLY	169

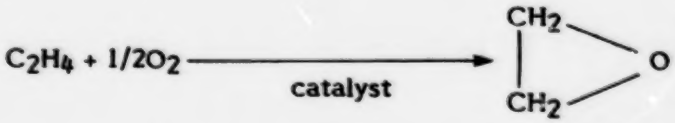
3.5 Future Development (Corpus 1983; CCP 1981)

Union Carbide Canada is planning a world-scale (225 kt/yr) glycol plant at Prentiss, Alberta. Production is slated for late 1984. Dow's Sarnia plant was scheduled to be closed in 1984.

3.6 Manufacture of Ethylene Oxide (Kirk-Othmer 1980; Shreve 1977)

3.6.1 General. Ethylene oxide is most commonly produced through the direct oxidation process using ethylene as the primary feedstock.

3.6.2 Manufacturing Process. The process involves the oxidation (by air or oxygen) of ethylene. This is represented by the following equation:



The reaction is carried out over a silver-based catalyst.

3.7 Major Uses in Canada (Corpus 1983; Celanese PB 1978)

Ethylene oxide is used in the manufacture of various grades of ethylene glycols and in the production of glycol ethers/polyglycols, ethanolamines and ethoxylates. It is also used to accelerate the maturing of tobacco leaves, in agricultural fungicides, as surface active agents, and as modifier for starch in the pulp and paper industry. In 1982, 73 percent of domestic production was used for making ethylene glycols, 10 percent was exported, 6 percent was used for ethoxylate production, and 6 percent was used in the production of glycol ethers/polyglycols.

3.8 Major Buyers in Canada (Corpus 1983)

Alkaril Chemicals, Mississauga, Ont.
Becton Dickenson Canada, Mississauga, Ont.
C-I-L, McMasterville, Que.
Canadian Alcolac, Valleyfield, Que.
Canadian Liquid Air, Toronto, Ont.
Chinook Chemical, Sarnia, Ont.
Domtar (CDC), Longford Mills, Ont.
Griffith Laboratories, Scarborough, Ont.
Hart Chemical, Guelph, Ont.
St. Lawrence Starch, Mississauga, Ont.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 General. Ethylene oxide is transported as a liquid under pressure in railway tank cars, cylinders, and drums. Tank motor vehicles are seldom used to transport ethylene oxide in Canada; such a method of transportation is not directly approved and requires transport authority exemption (Dow TED 1978).

4.1.2 Cylinders. Cylinders are of steel construction with a net mass of 0.45 to 454 kg (1 to 1000 lb.) (RTDCR 1974; MCA 1971). Cylinders must comply with specifications as described in Table 2.

TABLE 2 CYLINDER SPECIFICATIONS

CTC/DOT* Specification Number	Description
3B300	Seamless steel cylinder. Minimum service pressure 1035 kPa (150 psi), maximum 2070 kPa (300 psi). Maximum water capacity 454 kg (1000 lb.).
4B400	Welded and brazed steel cylinder. Longitudinal seams must be forged, lap-welded or brazed. Maximum water capacity 454 kg (1000 lb.). Minimum service pressure 1035 kPa (150 psi). Maximum service pressure 2760 kPa (400 psi).
4BA500	Welded or brazed steel cylinder of definitely prescribed steels. Maximum water capacity 454 kg (1000 lb.). Maximum service pressure 1550 kPa (225 psi). Maximum service pressure 3450 kPa (500 psi).
3E1800	Seamless steel cylinder. Maximum outside diameter 51 mm (2 in.). Maximum length 610 mm (2 ft.). Service pressure 12 400 (1800 psi).

* Canadian Transport Commission and Department of Transportation (U.S.)

4.1.3 Railway Tank Cars. Cars must comply with specifications 105A100W or 111A100W4 described in Table 3 (RTDCR 1974; TCM 1979). A typical railway tank car is illustrated in Figure 7; Table 4 indicates railway tank car details associated with this drawing.

TABLE 3 RAILWAY TANK CAR SPECIFICATIONS

CTC/DOT* Specification Number	Description
105A100W	Steel fusion-welded tank with manway nozzle. Insulated. Top unloading arrangement required. Safety valve (518 kPa) (75 psi). Bottom outlet or washout prohibited.
111A100W4	Steel fusion-welded tank without dome. Insulated. Gauging device. Top unloading arrangement required. Safety valve (518 kPa) (75 psi). Bottom outlet or washout prohibited.

* Canadian Transport Commission and Department of Transportation (U.S.)

Cars are equipped for unloading by pump or inert gas from the top of car only (Dow TED 1978). Air pressure must not be used for unloading (MCA 1971). Under the liquid unloading connection valve is an eduction pipe fastened to the manway cover plate and extending to the bottom of the tank. At the top of each eduction pipe, immediately below the manway cover plate, is a rising-ball, excess-flow valve designed to close when the rate of flow exceeds about 3180 kg/h (7000 lb./h). This is a protective device designed to close automatically against the flow if the connection valve is broken off or, under certain conditions, if the unloading line is severed (MCA 1971).

4.1.4 Drums. Insulated drums fabricated of lagged steel and with a maximum capacity of 227 L (50 gal.) may be used. The safe working pressure of this drum is 345 kPa (50 psi) (MCA 1971; RTDCR 1974). The CTC/DOT specification is 5P and the net weight is 180 kg (400 lb.) maximum. Drums are equipped with straight dip tubes which extend to the bottom for the removal of liquid ethylene oxide. The drum is pressurized to a maximum of 345 kPa (50 psi) with an inert gas to unload product (Matheson 1980; Kirk-Othmer 1980).

4.2 Off-loading

4.2.1 Off-loading Equipment and Procedures for Cylinders. The following points should be observed when handling and storing cylinders (MCA 1971):

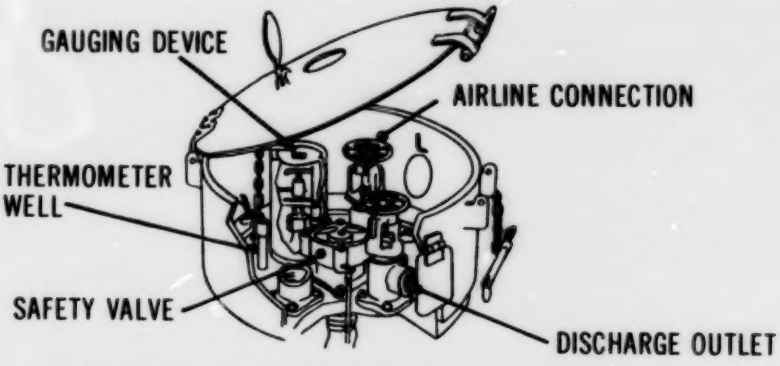
- Valve protection hoods should be in place.
- Containers should not be stored near ventilating systems.

FIGURE 7

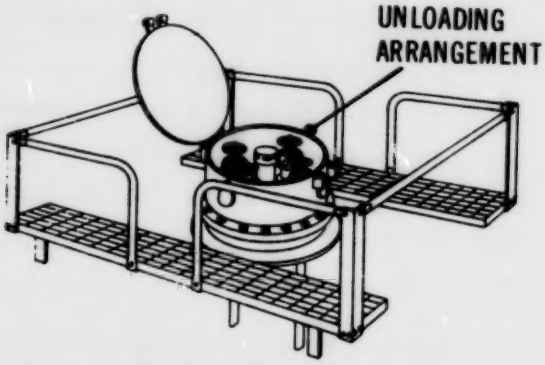
ETHYLENE OXIDE

RAILWAY TANK CAR CLASS 105A100W

Reference: RTDCR 1974; TCM 1979



Detail of top unloading arrangement



Detail of loading platform

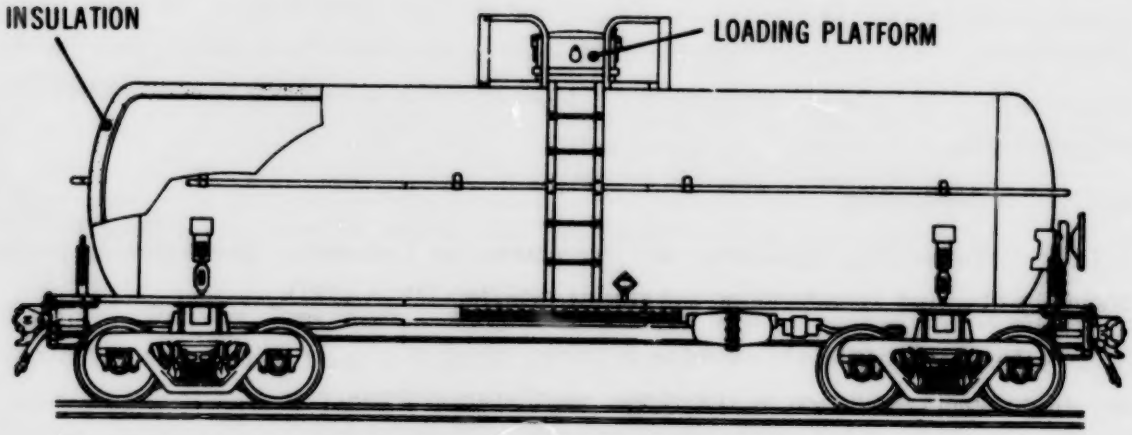


Illustration of tank car layout

TABLE 4 TYPICAL RAILWAY TANK CAR SPECIFICATIONS - CLASS 105A100W (RTDCR 1974; TCM 1979)

Description	Tank Car Size (Imp. Gal.) 9000		21 000		28 000	
Overall						
Nominal capacity	41 000 L	(9000 gal.)	95 000 L	(21 000 gal.)	127 000 L	(28 000 gal.)
Car weight - empty	30 300 kg	(66 800 lb.)	40 800 kg	(90 000 lb.)	50 800 kg	(112 000 lb.)
Car weight - max.	80 300 kg	(177 000 lb.)	83 500 kg	(184 000 lb.)	119 000 kg	(263 000 lb.)
Tank						
Material	steel		steel		steel	
Thickness (minimum)	14.3 mm	(9/16 in.)	14.3 mm	(9/16 in.)	14.3 mm	(9/16 in.)
Inside diameter	2.2 m	(88 in.)	2.4 m	(95 in.)	3.0 m	(120 in.)
Test pressure	690 kPa	(100 psi)	690 kPa	(100 psi)	690 kPa	(100 psi)
Burst pressure	3450 kPa	(500 psi)	3450 kPa	(500 psi)	3450 kPa	(500 psi)
Approximate Dimensions						
Coupled length	13 m	(42 ft.)	20 m	(65 ft.)	20 m	(67 ft.)
Length over strikers	12 m	(40 ft.)	19 m	(63 ft.)	20 m	(64 ft.)
Length of truck centres	9 m	(29 ft.)	16 m	(52 ft.)	16 m	(53 ft.)
Height to top of grating	4 m	(12 ft.)	4 m	(12 ft.)	4 m	(12 ft.)
Overall height	5 m	(15 ft.)	5 m	(15 ft.)	5 m	(15 ft.)
Overall width	3.2 m	(127 in.)	3.2 m	(127 in.)	3.2 m	(127 in.)
Length of grating	2 to 3 m	(7 to 10 ft.)	2 to 3 m	(7 to 10 ft.)	2 to 3 m	(7 to 10 ft.)
Width of grating	1.5 to 2 m	(5 to 6 ft.)	1.5 to 2 m	(5 to 6 ft.)	1.5 to 2 m	(5 to 6 ft.)
Loading/Unloading Fixtures						
Unloading connection	51 mm (2 in.) via valve and 76 mm (3 in.) check valve;					
Gauging Device	Float-type gauging or magnetic device and thermometer well					
Safety Devices	Safety relief valve set at 1550 kPa (75 psi), many cars equipped with shelf couplers and head shields. Some cars also equipped with tanks of 13 mm (1/2 in.) steel					
Insulation	51 to 152 mm (2 to 6 in.) fibreglass or cork insulation					

- Store to minimize external corrosion.
- Store cylinders upright.
- Store full and empty containers separately.

A water bath heated to a maximum of 50°C is used to empty the cylinder by the internal vapour pressure. Check valves must be installed in feed lines from the cylinder to prevent the reactants from entering the cylinder (MCA 1971). A flexible stainless steel tubing connection capable of withstanding a pressure of 4140 kPa (600 psi) should be installed between the container and the piping system (Dow TED 1978).

4.2.2 Off-loading Equipment and Procedures for Railway Tank Cars. Railway tank cars may be off-loaded only after the following precautionary steps have been undertaken (MCA 1971; Union Carbide):

- Unloading operations to be performed only by properly instructed personnel.
- Dead-end siding used only for ethylene oxide rail cars to be provided.
- Brakes must be set, wheels chocked and a proper derail employed.
- Suitable operating platform to be provided at unloading point.
- Tank car must be grounded.
- Eye protection and respirators or breathing apparatus should be worn.

The railway tank car may be unloaded by inert gas pressure or by pump (Dow TED 1978). No heat should be applied to the tank car. An inert gas line should be attached to the appropriate valve on top of the railway tank car to provide a pressure of 242 to 450 kPa (35 to 65 psi) for transfer of the oxide from the car to the receiving tank. Cylinder nitrogen is often used as the pressuring medium.

When a pump is utilized, a pressure of at least 242 kPa (35 psi) must be maintained to keep the vapour phase of the tank car in a nonexplosive range. Pressures above 242 kPa (35 psi) are necessary when unloading at temperatures above 30°C.

4.2.3 Specifications and Materials for Off-loading Equipment. Under this section, the components of a typical off-loading system at commonly employed temperatures and pressures will be discussed. These include piping, flanges and fittings, flexible connections, pumps, valves, gaskets, vaporizers and storage tanks.

Piping should be of carbon or stainless steel and hydrostatically tested to a pressure of at least 1550 kPa (225 psi). Copper piping, fittings or equipment should never be used for ethylene oxide service, since the possibility of failure is greater with such materials and the consequences of failure are likely to be serious (MCA 1971).

Pipeline joints should preferably be flanged or welded. If threaded joints are necessary, extreme care must be taken to obtain clean, sharp pipe threads, in order to ensure pressure-tight joints. A small amount of fluorinated hydrocarbon lubricant is recommended as a pipe dope. The dope should be applied to the male thread only in such a manner as to prevent its entrance into the piping system. Liquid ethylene oxide lines between shut-off valves should be provided with a relief valve (MCA 1971). All pipes should be bonded and grounded (CCPA 1983).

Flexible connectors consisting of a loop of stainless steel tubing should be installed between containers and rigid piping systems (Dow TED 1978). Hoses constructed of polytetrafluoroethylene (Teflon) may also be used, particularly at railway tank cars (MCA 1971).

Centrifugal or positive displacement pumps may be used for transfer of liquid ethylene oxide, complete with a minimum flow by-pass valve on the pump discharge line. Pumps should be provided with a high temperature kick-out switch. Running pumps against closed valves should be avoided. Pump motors must be explosion-proof (MCA 1971).

Valves fabricated from carbon or stainless steels may be of gate, globe, plug or ball types (MCA 1971). Gaskets should be spiral wound stainless steel with Teflon inserts (Dow TED 1978). Asbestos gaskets are attacked by liquid ethylene oxide and should never be employed (MCA 1971).

Ethylene oxide is converted from the liquid to the gaseous state by use of a vaporizer - a device consisting essentially of an evaporating manifold constructed of stainless steel pipe surrounded by a jacket through which hot water or low pressure (104 kPa) (15 psi) steam is passed. The liquid enters the manifold and vaporizes instantly. Automatic shut-down of heat and feed should be provided for in case of temperature increases greater than 20°C (MCA 1971).

Storage tanks should be designed in accordance with ASME codes regarding minimum design pressures consistent with the blanket gas pressures needed to maintain the vapour space nonexplosive. Design pressure of 518 kPa (75 psi) with blanket gas pressure of 483 kPa (65 psi) is normally used. Pressure relief valves are required (MCA 1971). Storage pressure must increase as the temperature increases to keep the vapour below the explosive limit.

4.3 Compatibility with Materials of Construction

The compatibility with materials of construction is indicated in Table 5. The unbracketed abbreviations are described in Table 6. The rating system for this report is briefly described below.

Recommended: This material will perform satisfactorily in the given application.

Conditional: Material will show deterioration in the given application; however, it may be suitable for intermittent or short-term service.

Not Recommended: Material will be severely affected in this application and should not be used.

TABLE 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

	Chemical		Material of Construction		
Application	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings	Most	Most	Carbon Steel Stainless Steel (Kirk-Othmer 1980)		PVDC (DCRG 1978) PE PVC I (MWPP 1978) Aluminum (Kirk-Othmer 1980)
		23			PVC I PVC II (DPPED 1967)
	5% Aqueous	66	Chlorinated Polyether (DCRG 1978)		
		93	PVDF (DCRG 1978)		Mercury Copper Silver Magnesium SS 416, SS 442 (MCA 1971)
2. Valves	Most	Most	Alloy 20 SS 300 series Nickel Alloys (MCA 1971)		

TABLE 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
3. Pumps	Most	Most	Alloy 20 SS 300 series Nickel Alloys (MCA 1971)		
4. Storage	Most	Most	Alloy 20 Nickel Alloys CS SS 300 series Pure Aluminum (MCA 1971)		Aluminum (Kirk-Othmer 1980)
5. Others	Technically Pure Liquid	-20	POM NR (GF)	CSM (GF)	uPVC, PE PP, NBR IIR, EPDM CR, FPM (GF)
		22			PVC (TPS 1978)
		66	PVDF (TPS 1978) NR, SBR CR, IIR EPDM (GPP)		NBR (GPP)
	100%	24 to 149	Glass (CDS 1967)		NR Asbestos (MCA 1971)
		24 to 71	Concrete (CDS 1967) PTFE Glass CFE (MCA 1971)		

TABLE 6 MATERIALS OF CONSTRUCTION

Abbreviation	Material of Construction
	Alloy 20
	Aluminum (pure)
	Chlorinated Polyether
CFE	Chlorotrifluoroethylene
CR	Polychloroprene (Neoprene) Rubber
CS	Carbon Steel
CSM	Chlorosulphonated Polyethylene (Hypalon)
EPDM	Ethylene Propylene Rubber
FPM	Fluorine Rubber (Viton)
	Glass
IIR	Isobutylene/Isoprene (Butyl) Rubber
NBR	Acrylonitrile/Butadiene (Nitrile, Buna N) Rubber
NR	Natural Rubber
	Nickel-Molybdenum (Hastelloy Alloy C)
PE	Polyethylene
POM	Polyoxymethylene
PP	Polypropylene
PTFE	Polytetrafluoroethylene (Teflon)
PVC (followed by grade)	Polyvinyl Chloride
PVDC	Polyvinylidene Chloride
PVDF	Polyvinylidene Fluoride
SS (followed by grade)	Stainless Steel
SBR	Styrene-Butadiene (GR-S, Buna S) Rubber
uPVC	Unplasticized Polyvinyl Chloride

5 CONTAMINANT TRANSPORT

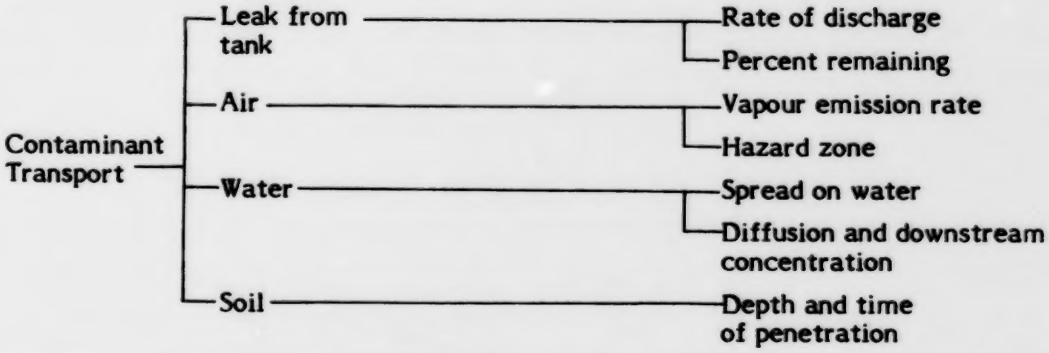
5.1 General Summary

Ethylene oxide is commonly transported in tank cars as a liquid under pressure. When spilled in the environment, it will form a liquid pool, spreading on the surface of a water body or on the ground. A flammable, irritating vapour is released rapidly from the pool to the atmosphere by evaporation.

When spilled on water, some of the ethylene oxide will mix and the rest will evaporate to the atmosphere. The vapour cloud tends to hug the surface and spread rather than lift and disperse.

Ethylene oxide spills on soil surfaces will partly vaporize and partly adsorb onto the soil at a rate dependent on the soil type and its degree of saturation with water. Downward transport of the liquid toward the groundwater table may cause environmental concerns.

The following factors are considered for the transport of spill in the air, water and soil media:



5.2 Leak Nomograms

5.2.1 Introduction. Ethylene oxide is commonly transported as a liquid under pressure at ambient temperature. While the capacities of the railway tank cars vary widely, one size has been chosen throughout the EnviroTIPS series for development of the leak nomograms. It is approximately 2.75 m in diameter and 13.4 m long, with a carrying capacity of about 80 000 L.

If a tank car loaded with ethylene oxide is punctured on the bottom, all of the contents will drain out. The instantaneous discharge rate (q) is a function of the height of

the fluid above the hole (H), the internal pressure of the tank (P), the hole size (A) and shape, and a coefficient of discharge (C_d). For the purposes of nomogram preparation, a constant discharge coefficient of 0.8 has been assumed.

If the tank car is punctured in the top or at any point above the liquid level, gas will be vented until all of the liquid has vaporized and the internal and external tank pressures have equalized. For the purposes of nomogram preparation, the liquid is assumed to remain at a constant temperature (isothermal) equal to the ambient temperature (T). Consequently, the venting rate (q) is assumed to be constant until all of the liquid is vaporized. The venting rate is a function of the internal tank pressure (P), which is equal to the saturated vapour pressure (P_{sat}) of the liquid at temperature T. The assumed maximum tank ambient temperature is 40°C, yielding a saturated vapour pressure (P_{sat}) of 285 kPa.

The assumption of isothermal conditions will maximize the gas release rate from the tank and will be conservative for most cases. In most spill circumstances, approximately 20 percent of the vapour will flash off after the accident. Evaporative cooling will subsequently reduce the evaporation rate. This subsequent (i.e., after the initial vapour release) emission rate may be up to 3 or 4 orders of magnitude slower depending on the ambient temperature, amount of insulation lost, and position of the tank car (e.g., on the ground, partially in water, etc.).

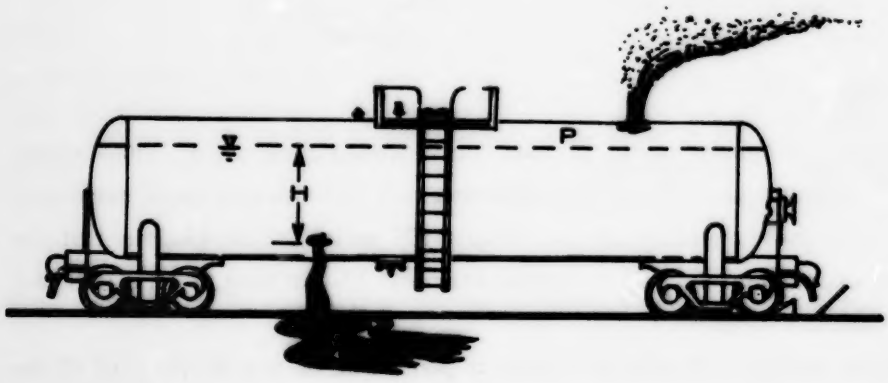


FIGURE 8 TANK CAR WITH PUNCTURE HOLE IN BOTTOM OR TOP

The aim of the nomograms is to provide a simple means to obtain the time history of the venting process. This may include venting from a bottom puncture (liquid release) or from a puncture above the liquid level (gas venting). The details of the models used to calculate venting rates are described in the Introduction Manual.

5.2.2 Nomograms.

5.2.2.1 Bottom puncture - liquid venting.

Figure 9: Percent remaining versus time. Figure 9 provides a means of estimating the percent of ethylene oxide remaining in the standard tank car after the time of puncture for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

The standard tank car is assumed to be initially full (at t=0) with a volume of about 80 000 L of ethylene oxide at 40°C. The amount remaining at any time (t) is not only a function of the discharge rate over time, but also of the size and shape of the tank car.

Figure 10: Discharge rate versus puncture size. Figure 10 provides a means of estimating the maximum discharge rate (L/s) for a number of equivalent hole diameters. As the pressure force dominates the gravitational force, the discharge rate remains relatively constant as the tank empties.

5.2.2.2 Top puncture - gas venting.

Figure 11: Percent remaining versus time. Figure 11 provides a means of estimating the percent of ethylene oxide remaining in the standard tank car after the time of puncture for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

Figure 12: Discharge rate versus puncture size. Figure 12 presents the relationship between discharge rate (kg/s) and the equivalent diameter of the hole for gas venting above the liquid level in the tank car. For any one hole size, the venting rate will be constant until all the liquid is vaporized. This is consistent with the assumption of isothermal conditions in the tank and results in a conservative estimate of the gas venting rate.

The values presented in Figure 12 are independent of the tank car size, but assume that the temperature of the liquid is 40°C, yielding a saturated vapour pressure of 285 kPa.

FIGURE 9

ETHYLENE OXIDE

PERCENT REMAINING vs TIME

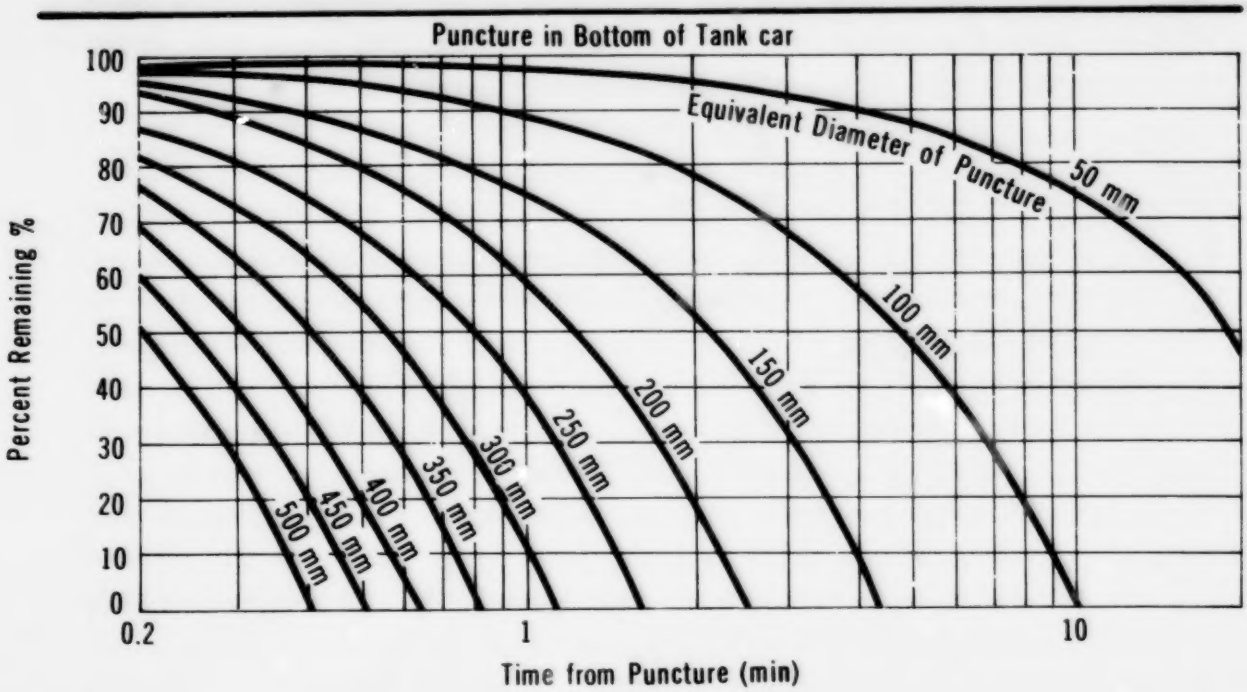


FIGURE 10

ETHYLENE OXIDE

DISCHARGE RATE vs PUNCTURE SIZE

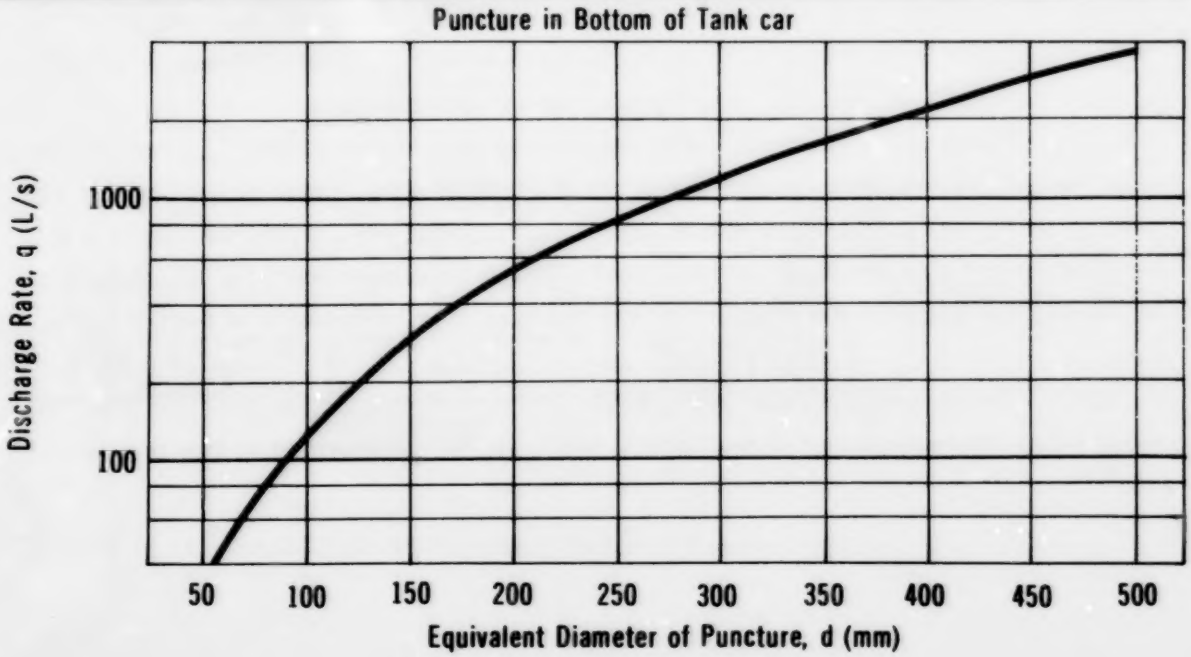


FIGURE 11

ETHYLENE OXIDE

PERCENT REMAINING vs TIME

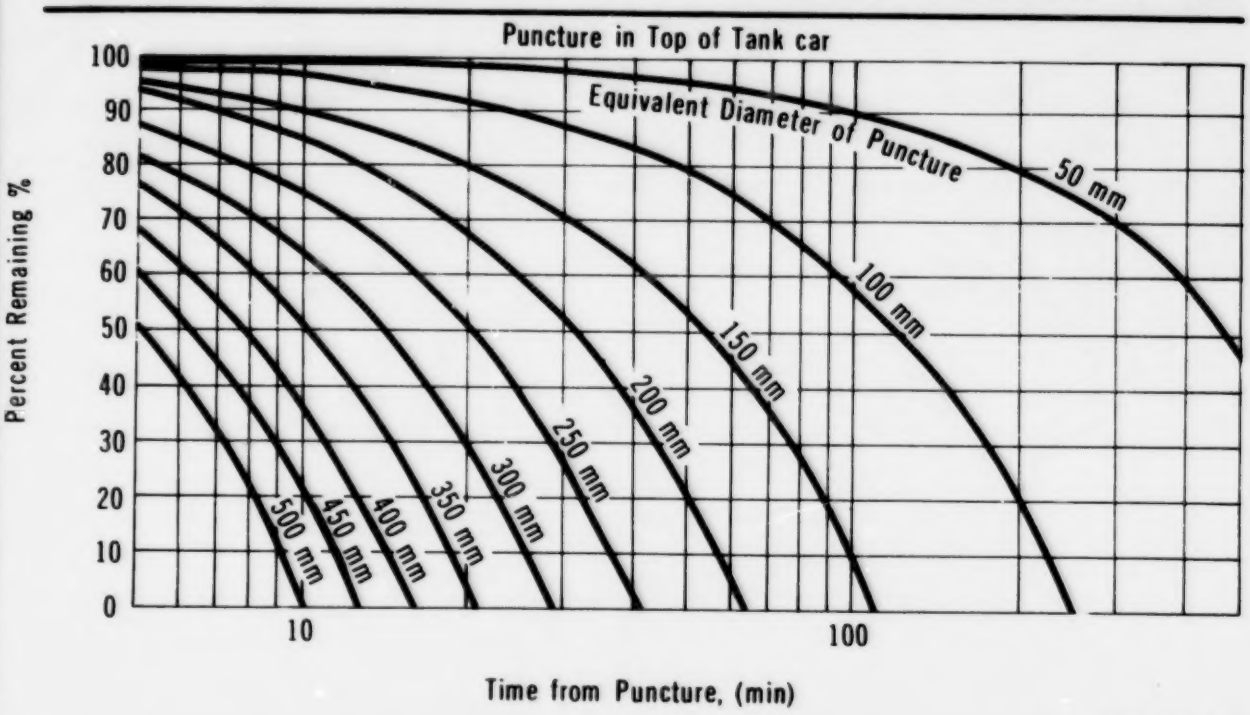
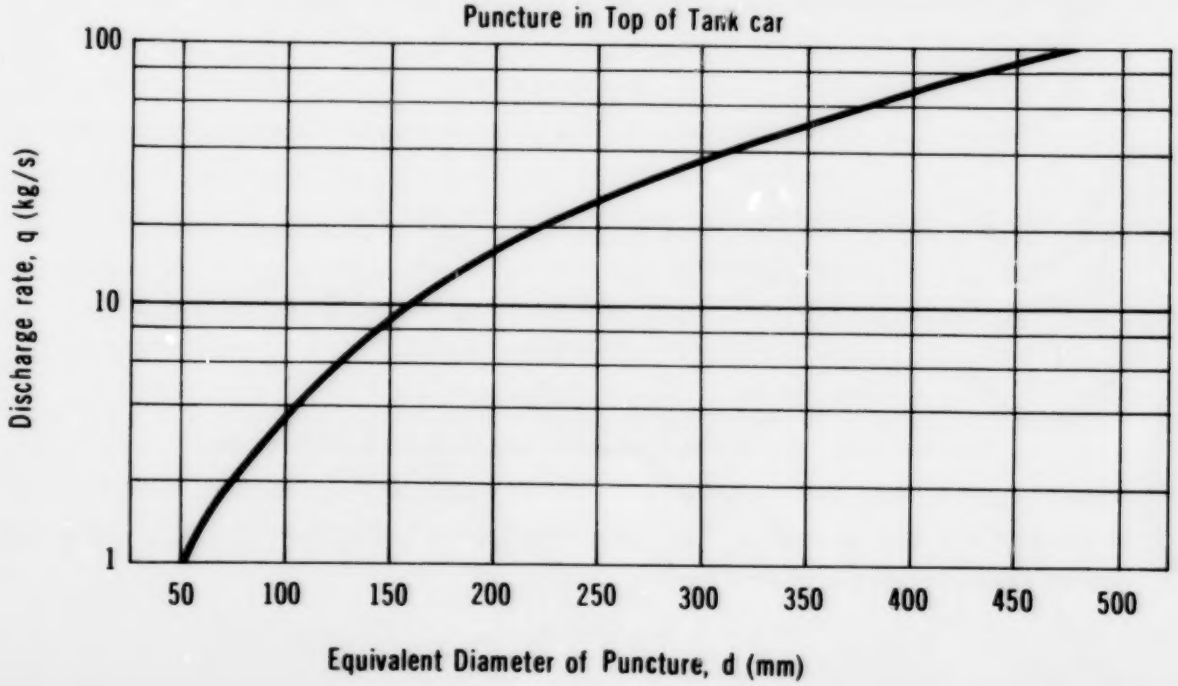


FIGURE 12

ETHYLENE OXIDE

DISCHARGE RATE vs PUNCTURE SIZE



5.2.3 Sample Calculations.

i) Problem A

The standard tank car filled with ethylene oxide at 40°C has been punctured on the bottom. The equivalent diameter of the hole is 150 mm. What percent of the initial 80 000 L remains after 2 minutes and what is the instantaneous discharge rate from the tank?

Solution to Problem A

Step 1: Calculate the amount remaining at t=2 min

- Use Figure 9
- With t=2 min and d=150 mm, the amount remaining is about 53 percent or 42 500 L

Step 2: Calculate the discharge rate

- Use Figure 10
- With d=150 mm, the instantaneous discharge rate (q) = 300 L/s

ii) Problem B

The standard tank car in Problem A has been punctured above the liquid level. The equivalent diameter of the orifice is estimated at 250 mm. How long will it take to empty the tank car and what is the release rate, assuming isothermal conditions?

Solution to Problem B

Step 1: Calculate the time to empty

- Use Figure 11
- With d=250 mm, the tank empties (0 percent remaining) in approximately 40 min

Step 2: Calculate the discharge rate

- Use Figure 12
- With d=250 mm and assuming isothermal conditions, the venting rate is constant at 25 kg/s

5.3 Dispersion in the Air

5.3.1 Introduction. Since ethylene oxide under pressure is a volatile liquid, vapour released from a liquid pool spilled on a ground or water surface vaporizes rapidly enough to consider the spill as producing instantaneous vapour in the form of a puff. Only this type of vapour release is treated here.

To estimate the vapour concentrations downwind of the accident site for the determination of the flammability or toxicity hazard zone, the atmospheric transport and dispersion of the contaminant vapour must be modelled. The models used here are based on Gaussian formulations and are the ones most widely used in practice for contaminant concentration predictions. The model details are contained in the Introduction Manual.

Figure 13 depicts schematically the contaminant plume configuration from a "puff" surface release. The dispersion model represents the spill as an instantaneous point source (with a total vapour release quantity, Q_T) equal to the amount of contaminant spilled.

Although no relevant spill information is available on the behaviour of a cloud of ethylene oxide gas, it is expected that in the initial period immediately after the spill, the cloud will behave as a denser-than-air gas. This is due primarily to the greater density of ethylene oxide gas (1.5 times that of air of 20°C) and due to the fact that the vapour cloud arising from the cold bulk liquid will be cold itself. Ground hugging and gas accumulation in low-lying areas may therefore be observed during the initial period. Conventional Gaussian modelling will tend to depict heavier-than-air plumes (puffs) to be narrower than observed.

Since the boiling point of liquid ethylene oxide is low for a liquefied gas (11°C at 1 atm), spills on a ground surface at low temperatures (about 0°C and less) will result in considerable overestimation since the vapour emission rate would not approach that of a puff release situation and worst case values would be provided. For this reason it will be assumed that only 25 percent of the instantaneously spilled ethylene oxide will produce an instantaneous vapour puff. It is recognized that although 75 percent of the ethylene oxide remains and poses a potential source of hazard, the vapour emission rate will be small in comparison to the initial puff release. Also, the hazard zone determined for the initial puff release will provide conservative estimates.

5.3.2 Vapour Dispersion Nomograms and Tables. The aim of the air dispersion nomograms is to define the hazard zone due to toxicity or flammability of a vapour cloud. The following nomograms and data tables are contained in this section (to be used in the order given):

Figure 15: normalized vapour concentration as a function of downwind distance and weather conditions

Table 7: weather conditions

FIGURE 13

ETHYLENE OXIDE

SCHEMATIC OF CONTAMINANT PUFF

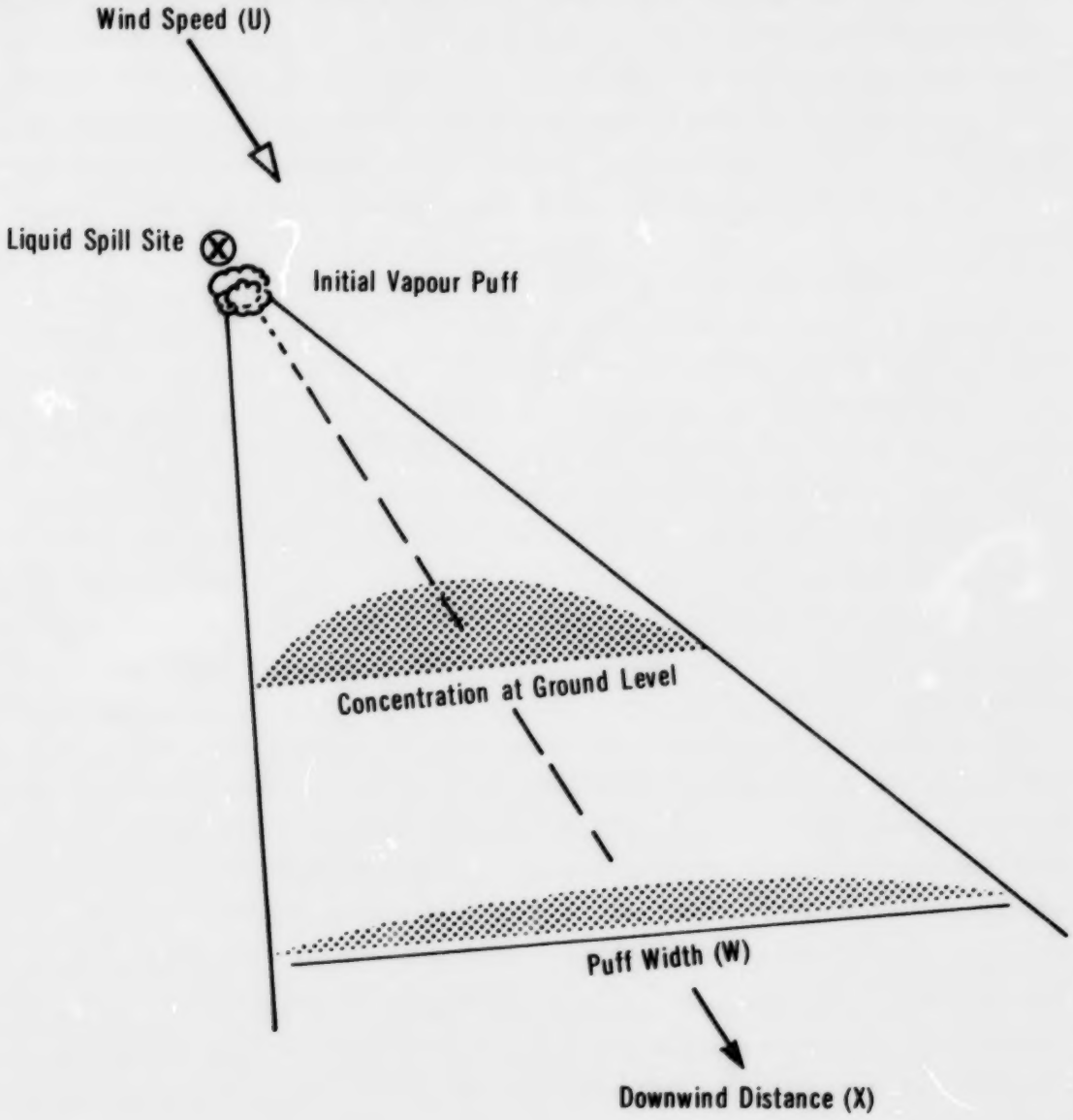


Table 8: maximum puff hazard half-widths

Figure 18: vapour puff travel distance as a function of time elapsed since the spill and wind speed

The flowchart given in Figure 14 outlines the steps necessary to make vapour dispersion calculations and identifies the nomograms or tables to be used. This section deals only with the portion contained within the dashed box. Data on "total liquid discharged" is contained in Section 5.2. A description of each vapour dispersion nomogram and its use follows.

5.3.2.1 Figure 15: Vapour concentration versus downwind distance. Figure 15 shows the relationship between the vapour concentration and the downwind distance for weather conditions D and F. The nomograms were developed using the dispersion models described in the Introduction Manual. The vapour concentration is represented by the normalized, ground-level concentration (C/Q_T) at the centreline of the contaminant puff. Weather condition F is the poorest for dispersing a vapour cloud and condition D is the most common in most parts of Canada. Before using Figure 15, the weather condition must be determined from Table 7.

TABLE 7 WEATHER CONDITIONS

Weather Condition F	Weather Condition D
Wind speed < 11 km/h (≈3 m/s) and one of the following - overcast day - night time - severe temperature inversion	Most other weather conditions

Use: The maximum hazard distance, X, downwind of the spill can be calculated from Figure 15 knowing:

- Q_T, the mass of vapour emitted (assumed equivalent to 25 percent of liquid spilled)
- U, the wind speed (m/s)
- the weather condition
- the hazard concentration limit, C, which is the lower value of 10 times the Threshold Limit Value (TLV●, in g/m^3), or the Lower Flammability Limit (LFL, in g/m^3). Note: To convert the TLV● (in ppm) and the LFL (in volume percent) to

FIGURE 14

ETHYLENE OXIDE

FLOW CHART TO DETERMINE VAPOUR HAZARD ZONE

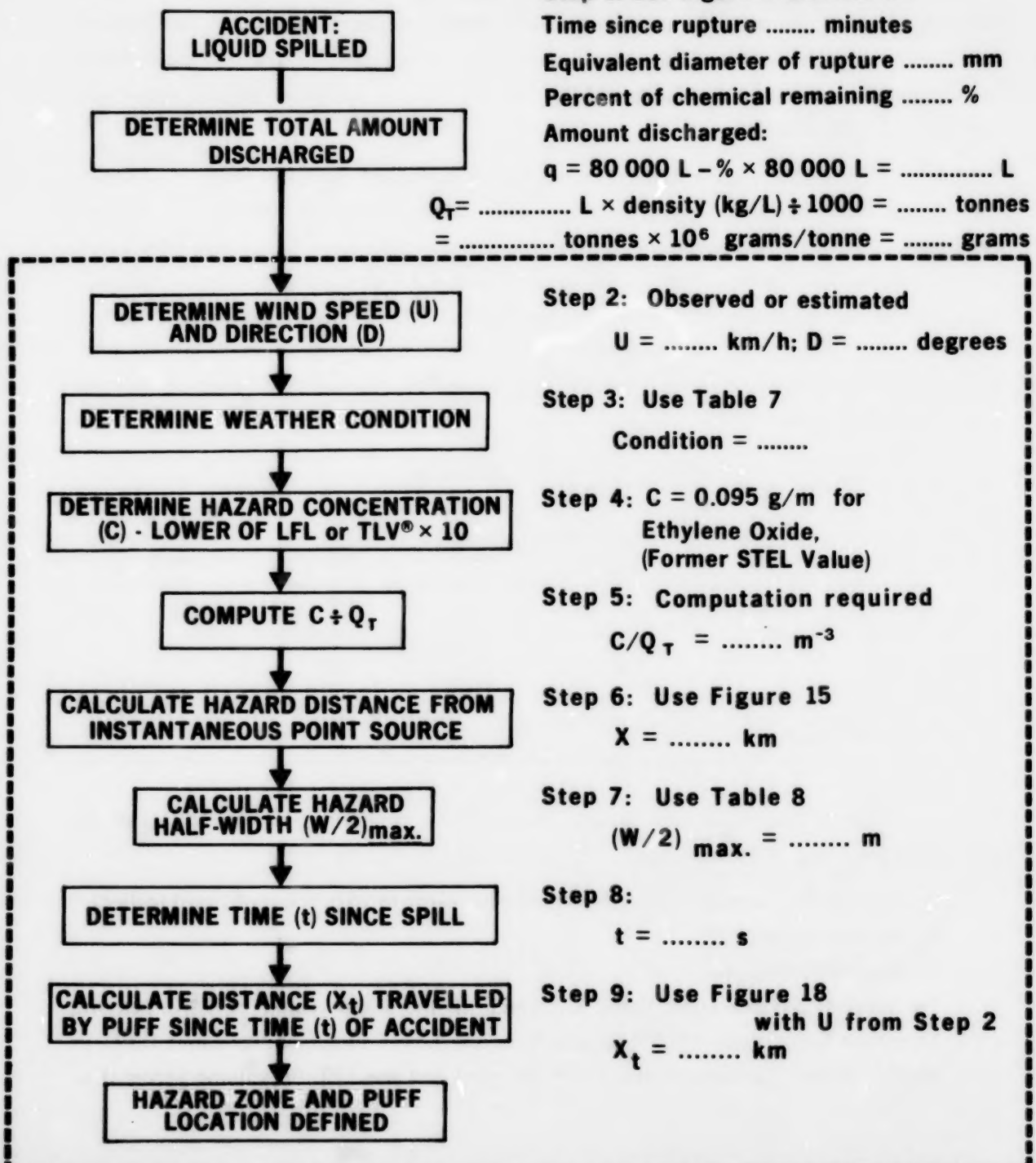
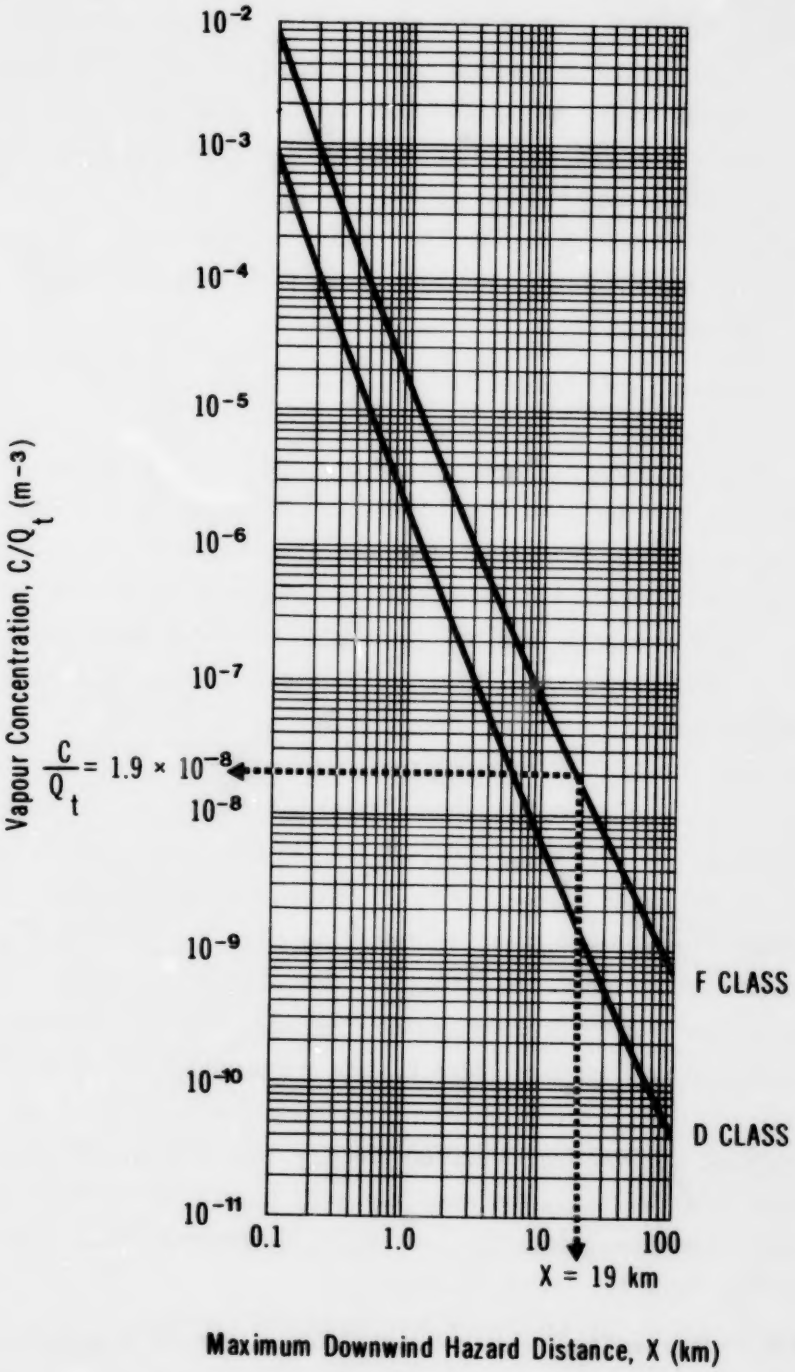

ACCIDENT: LIQUID SPILLED
DETERMINE TOTAL AMOUNT DISCHARGED
DETERMINE WIND SPEED (U) AND DIRECTION (D)
DETERMINE WEATHER CONDITION
DETERMINE HAZARD CONCENTRATION (C) - LOWER OF LFL or TLV® × 10
COMPUTE C ÷ Q_T
CALCULATE HAZARD DISTANCE FROM INSTANTANEOUS POINT SOURCE
CALCULATE HAZARD HALF-WIDTH $(W/2)_{max.}$
DETERMINE TIME (t) SINCE SPILL
CALCULATE DISTANCE (X_t) TRAVELLED BY PUFF SINCE TIME (t) OF ACCIDENT
HAZARD ZONE AND PUFF LOCATION DEFINED
Step 1: Use Figure 9 Section 5.2
Time since rupture ..... minutes
Equivalent diameter of rupture ..... mm
Percent of chemical remaining ..... %
Amount discharged:
q = 80 000 L – % × 80 000 L = ... L
Q_T = ... L × density (kg/L) ÷ 1000 = ... tonnes
= ..... tonnes × 10^6 grams/tonne = ... grams
Step 2: Observed or estimated
U = ... km/h; D = ... degrees
Step 3: Use Table 7
Condition = ...
Step 4: C = 0.095 g/m for Ethylene Oxide, (Former STEL Value)
Step 5: Computation required
C/Q_T = ... m^{-3}
Step 6: Use Figure 15
X = ... km
Step 7: Use Table 8
$(W/2)_{max.}$ = ... m
Step 8:
t = ... s
Step 9: Use Figure 18 with U from Step 2
X_t = ... km

FIGURE 15

ETHYLENE OXIDE

VAPOUR CONCENTRATION VS DOWNWIND DISTANCE



concentrations in g/m^3, use Figures 16 and 17. For this case, a value of 50 ppm has been chosen

A hazard concentration limit of 10 times the TLV• has been arbitrarily chosen for most EnviroTIPS manuals as it represents a more realistic level at which there would be concern for human health on the short term (i.e., on the order of 30 minutes). The TLV• is a workplace standard for long-term exposure; use of this value as the hazard limit would result in unrealistically large hazard zones. The value of 50 ppm is chosen in this manual as it represents 10 x 5 ppm, a former TLV• value, and also is directly equivalent to a former NIOSH ceiling value. Ten times the current TLV• of 1 ppm would result in very large evacuation zones.

5.3.2.2 Table 8: Maximum puff hazard half-widths. This table presents data on the maximum puff hazard half-width, $(W/2)_{max}$, for a range of Q_T values under weather conditions D and F. These data were computed using the dispersion modelling techniques given in the Introduction Manual for a value of 50 ppm ethylene oxide, or 0.095 g/m^3. The maximum puff hazard half-width represents the maximum half-width of the ethylene oxide vapour cloud, downwind of the spill site, corresponding to a hazard concentration limit of 10 x TLV•. Table 8 is therefore only applicable for an ethylene oxide hazard concentration limit of 0.095 g/m^3. Also, data are provided up to a maximum hazard distance downwind of 100 km.

Under weather condition D, the wind speed (U) range applicable is 1 to 30 m/s. The range of instantaneous vapour emission rates (Q_T) used was 0.01 to 3050 tonnes, respectively. If the entire contents of an 80 000 L (17 600 Imp. gal.) tank car spill, the mass spilled would be 69 500 kg, or approximately 70 tonnes. Therefore, under class D of Table 8, data are provided for up to 43 times this amount.

Under weather condition F, the wind speed (U) range applicable is 1 to 3 m/s. The range of instantaneous vapour emission rates (Q_T) used was 0.01 to 140 tonnes, respectively. Therefore, under class F of Table 8, data are provided for up to 2 times a standard rail car load.

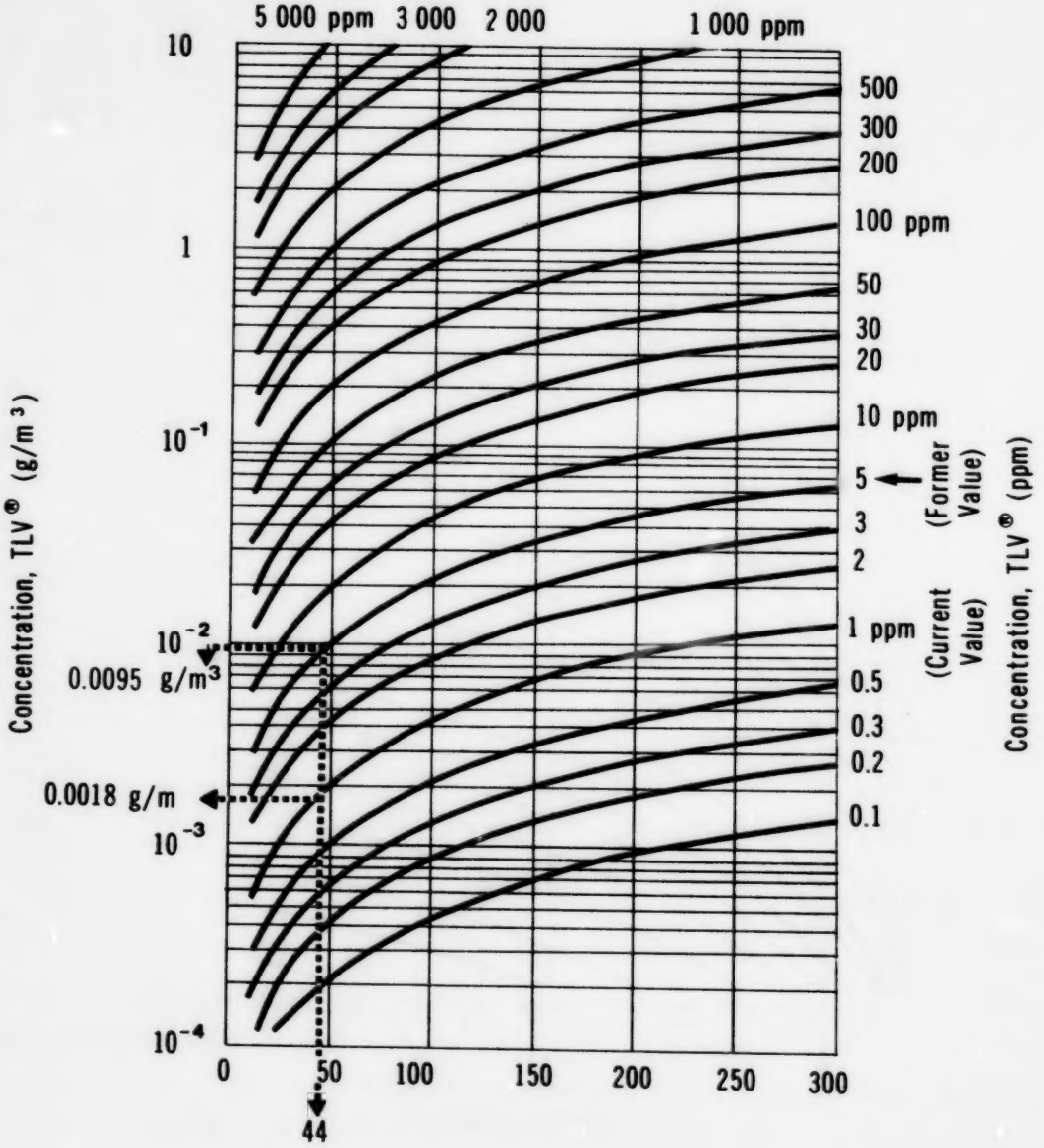
Use: Knowing the weather condition and Q_T, pick the closest value in the table and the corresponding $(W/2)_{max}$, the maximum puff hazard half-width, in metres. (For an intermediate value, interpolate Q_T and $(W/2)_{max}$ values.) Also refer to the example at the bottom of Table 8.

5.3.2.3 Figure 18: Puff travel time versus travel distance. Figure 18 presents plots of puff travel time (t) versus puff travel distance (X_t) as a function of different wind

FIGURE 16

ETHYLENE OXIDE

CONVERSION OF THRESHOLD LIMIT VALUE (TLV®) UNITS (ppm to g/m³)



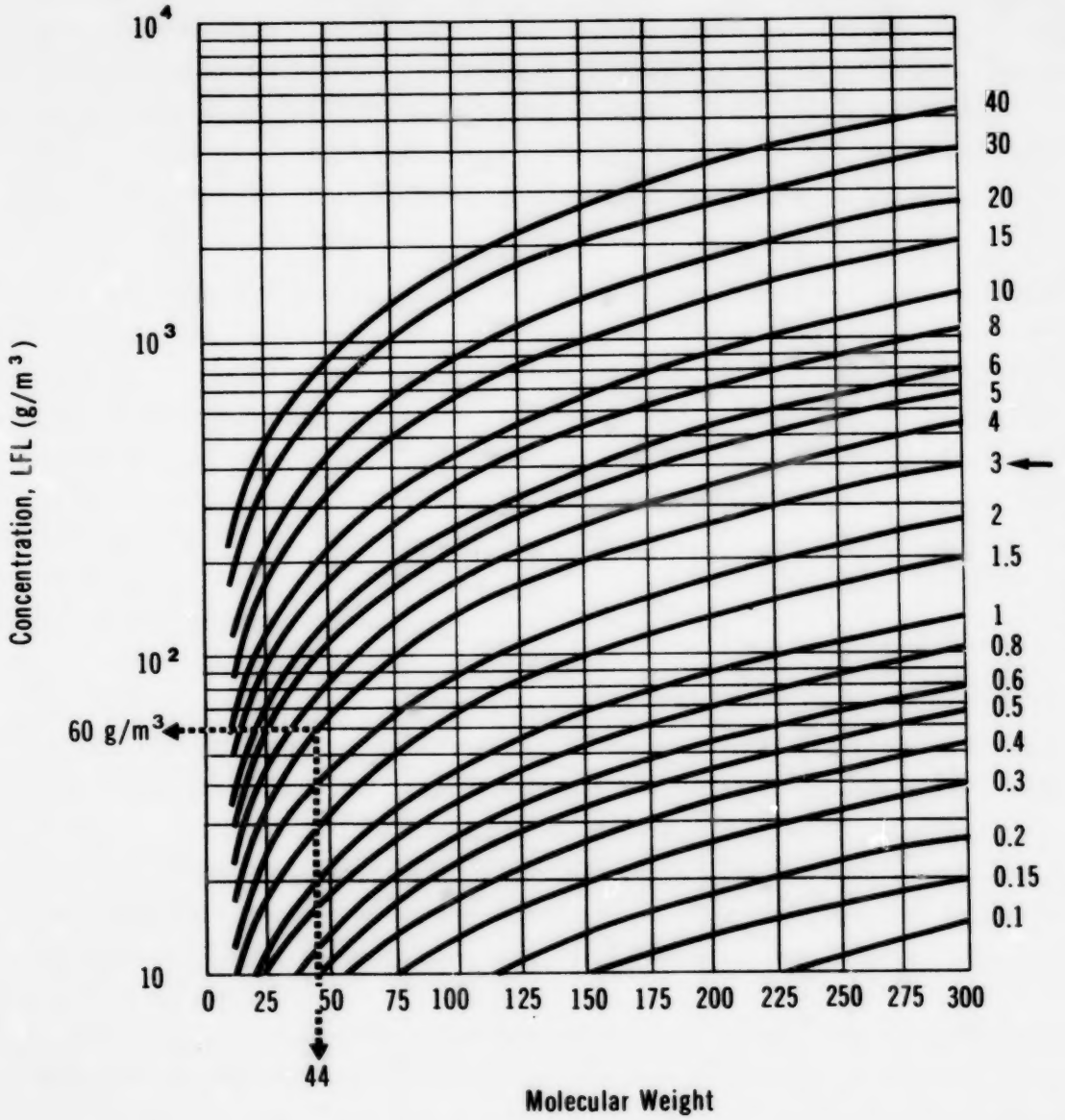
Example: ETHYLENE OXIDE, MW = 44, TLV® = 5 ppm, 1 ppm
then TLV® in g/m³ = 0.0095, 0.0018

Note: data applicable at 25°C and 760 mm Hg pressure

FIGURE 17

ETHYLENE OXIDE

CONVERSION OF LOWER FLAMMABILITY LIMIT (LFL) UNITS (volume % to g/m³)



Example: ETHYLENE OXIDE, MW = 44, LFL = 3% then LFL in g/m³ = 60

Note: data applicable at 25°C and 760 mm Hg pressure

TABLE 8 MAXIMUM PUFF HAZARD HALF-WIDTHS (FOR ETHYLENE OXIDE)

Weather Condition D			Weather Condition F		
Q'_T (tonnes)	$(W/2)_{max}$ (m)		Q_T (tonnes)	$(W/2)_{max}$ (m)	
3050	4025	(99.4 km)*	140	1850	(98.6 km)*
3000	4000		100	1600	
2500	3730		75	1415	
2000	3425		50	1190	
1500	3070		25	885	
1250	2860		20	805	
1000	2630		15	710	
750	2355		10	600	
500	2015		5	445	→ $(W/2)_{max}$ = 445 m
250	1550	Q_T = 5 tonnes →	2.5	340	
200	1420		1.0	240	
150	1270		0.5	180	
100	1090		0.1	100	
75	975		0.05	75	
50	835		0.01	40	
25	650				
20	600				
15	540				
10	465				
5	360				
2.5	280				
1	200				
0.5	155				
0.1	85				
0.05	65				
0.01	35				

* Data are provided up to a maximum downwind hazard distance of 100 km.

Example: Under weather condition F and Q_T = 5 tonnes, the puff hazard half-width $(W/2)_{max}$ = 445 m.

Note: Above table is valid only for an ethylene oxide concentration of 50 ppm, or 0.095 g/m^3.

speeds (U). This is simply the graphical presentation of the relationship $X_t = Ut$ for a range of typical wind speeds.

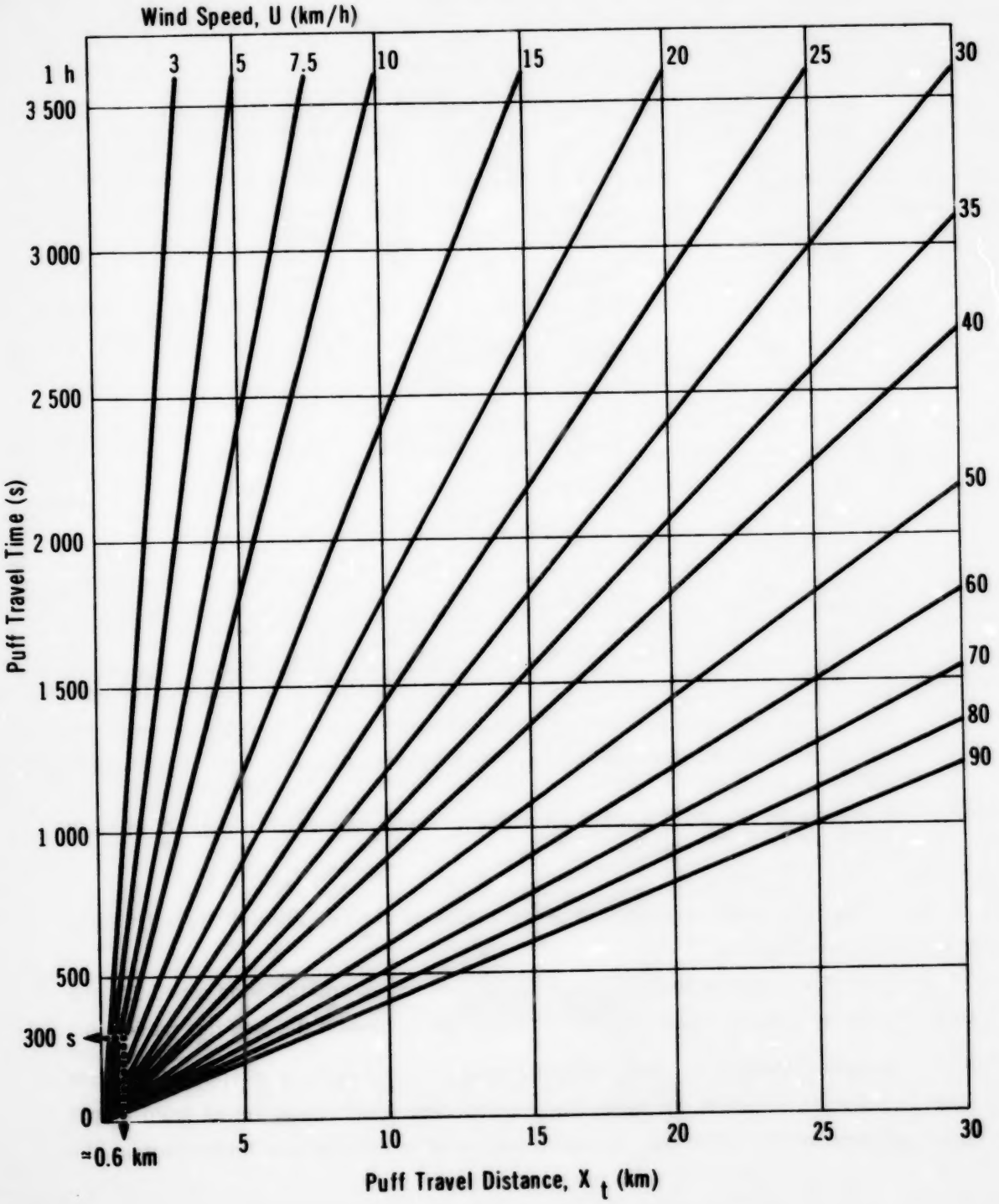
Use: Knowing the time (t) since the spill occurred and the wind speed (U), the distance (X_t) can be determined which indicates how far downwind the puff has travelled.

5.3.3 Sample Calculation. The following sample calculation is intended to outline the steps required to estimate the downwind hazard zone which could result from a spill of liquid ethylene oxide. The user is cautioned to take note of the limitations in the

FIGURE 18

ETHYLENE OXIDE

PUFF TRAVEL TIME VS TRAVEL DISTANCE



calculation procedures described herein and in the Introduction Manual. The estimates provided here apply only for conditions given. It is recommended that the user employ known or observational estimates (i.e., of the spill quantity) in a particular spill situation if possible.

Problem

During the night, at about 2:00 a.m., 20 tonnes of liquid ethylene oxide were spilled on a flat ground surface. It is now 2:05 a.m. The temperature is 20°C and the wind is from the NW at 7.5 km/h. Determine the extent of the vapour hazard zone.

Solution

Step 1: Quantity spilled is given, Q_T = 20 tonnes

- Q_T = 20 tonnes x 0.25 (assuming 25 percent instantaneous vapour) = 5 tonnes
- $Q_T = 5 \times 10^6$ g

Step 2: Determine the wind speed (U) and direction (D)

- Use available weather information, preferably on-site observations
- Given: U = 7.5 km/h, then U = 7.5 ÷ 3.6 = 2.1 m/s
  D = NW or 315° (D = Direction from which wind is blowing)

Step 3: Determine the weather condition

- From Table 7, weather condition = F since U is less than 11 km/h and it is night

Step 4: Determine the hazard concentration limit (C)

- This is the lower of 50 ppm, or the LFL (LFL = 60 g/m^3), so for ethylene oxide
  C = 0.095 g/m^3 (50 ppm)

Step 5: Compute C/Q_T

- $C/Q_T = \dfrac{0.095}{5 \times 10^6} = 1.9 \times 10^{-8}$ m^{-3}

Step 6: Calculate the hazard distance (X) from the instantaneous point source

- From Figure 15, with $C/Q_T = 1.9 \times 10^{-8}$ m^{-3} and weather condition F, X ≈ 19 km

Step 7: Calculate the puff hazard half-width $(W/2)_{max}$

- Use Table 8

- With Q_T = 5 tonnes
- Then for weather condition F, $(W/2)_{max}$ = 445 m

Step 8: Determine the time since the spill

- t = 5 min x 60 s/min = 300 s

Step 9: Calculate the distance travelled (X_t) by the vapour puff since the time of the accident

- Using Figure 18, with t = 300 s and U = 7.5 km/h, then X_t = 0.6 km (more accurately from X_t = Ut = 2.1 m/s x 300 s = 630 m = 0.63 km)

Step 10: Map the hazard zone

- This is done by drawing a rectangular area with dimensions of twice the maximum puff hazard half-width (445 m) by the maximum hazard distance downwind of the instantaneous point source (19 km) along the direction of the wind, as shown in Figure 19
- If the wind is reported to be fluctuating by 20° about 315° (or from 315° $\pm$ 10°), the hazard zone is defined as shown in Figure 20
- Note that the puff has only travelled 0.63 km in the 5 minutes since the spill. At a wind speed of 7.5 km/h there remain 147 minutes before the puff reaches the maximum downwind hazard distance of 19 km

5.4 Behaviour in Water

5.4.1 Introduction. When spilled on water, ethylene oxide will vaporize and at the same time spread on the surface and mix with the water. For the purpose of nomogram preparation, two worst case situations have been assumed. First, the extent of spread on the surface of the water has been estimated, assuming that none of the ethylene oxide is dissolved in the water. However, the loss due to vaporization has been taken into account. Secondly, the water pollution hazard has been evaluated by assuming all of the ethylene oxide is dissolved with water and no vaporization occurs. These two cases represent the worst case situations for the extent of spread of ethylene oxide on the surface of water and for the water pollution hazard associated with ethylene oxide dissolved in water.

5.4.2 Spreading on Water. The rate of spreading on water is based on the balance of forces tending to spread the liquid (gravity and surface tension) and those tending to resist spreading (inertial and viscous forces). Since high vapour pressure liquids such as ethylene oxide evaporate quickly, only the initial gravity-inertia regime of spread is considered

FIGURE 19

ETHYLENE OXIDE

HAZARD AREA FOR STEADY WINDS, EXAMPLE PROBLEM

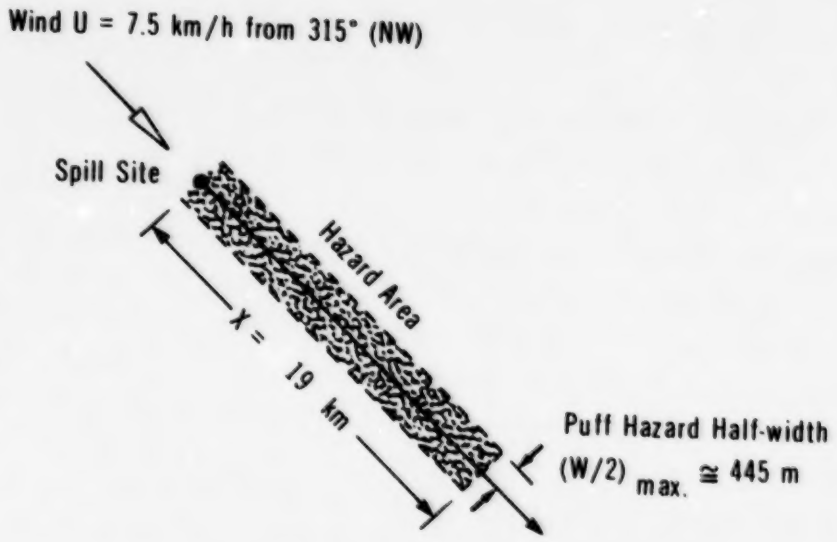
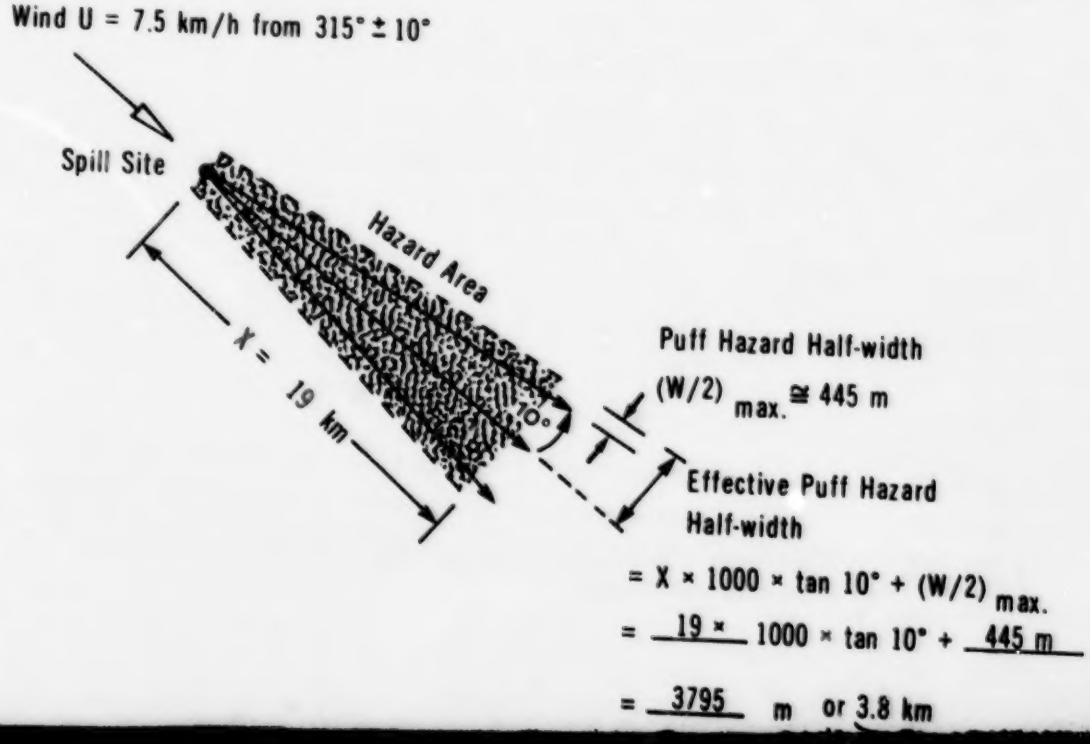


FIGURE 20

ETHYLENE OXIDE

HAZARD AREA FOR UNSTEADY WINDS , EXAMPLE PROBLEM


Wind U = 7.5 km/h from 315° ± 10°
Spill Site
Hazard Area
X = 19 km
10°
Puff Hazard Half-width
(W/2) max. ≅ 445 m
Effective Puff Hazard
Half-width
= X × 1000 × tan 10° + (W/2) max.
= 19 × 1000 × tan 10° + 445 m
= 3795 m or 3.8 km

relevant (Raj 1974). The maximum size of the spill pool depends to a large extent on the rate of vaporization.

The equations representing the spreading of the spill on water are presented in the Introduction Manual. For the purposes of the nomogram presented, the water temperature has been taken at 20°C, representing a reasonable maximum for surface water bodies. This condition maximizes the spill size. No dissolution is assumed for this case.

5.4.3 **Dissolution in Water.** For this condition, all of the spilled ethylene oxide is assumed to dissolve rapidly without any vaporization. Mixing takes place and the spill is diluted. This mixing can generally be described by classical diffusion equations with one or more diffusion coefficients. In rivers, the principal mixing agent is stream turbulence while in calm water mixing takes place by molecular diffusion.

To estimate pollutant concentration in a river downstream from a spill, the turbulent diffusion has been modelled. The one-dimensional model uses an idealized rectangular channel section and assumes a uniform concentration of the pollutant throughout the section. Obviously, this applies only to points sufficiently far downstream of the spill where mixing and dilution have distributed the pollutant across the entire river channel. The model is applicable to rivers where the ratio of width to depth is less than 100 ($W/d > 100$) and assumes a Manning's roughness coefficient of 0.03. Details of the model are outlined in the Introduction Manual.

No modelling has been carried out for molecular diffusion in still water. Rather, nomograms have been prepared to define the hazard zone and the average concentration within the hazard zone as a function of spill size, but independent of time.

5.4.4 **Nomograms.** The following nomograms are presented to calculate spreading on still water (without dissolution) and to estimate pollutant concentrations in non-tidal rivers and in lakes (without vaporization).

Spreading on Still Water

Figure 21: maximum spill radius versus spill size with estimated times for complete evaporation

Dissolution in Water - Non-tidal Rivers

Figure 23: time versus distance for a range of average stream velocities

Figure 24: channel width versus hydraulic radius for a range of stream depths

Figure 25: diffusion coefficient versus hydraulic radius for a range of average stream velocities

Figure 26: alpha* versus diffusion coefficient for various time intervals

Figure 27: alpha versus delta* for a range of spill sizes

Figure 28: maximum concentration versus delta for a range of river cross-sectional areas

Dissolution in Lakes or Still Water Bodies

Figure 29: volume versus radius for the hazard zone for a range of lake depths

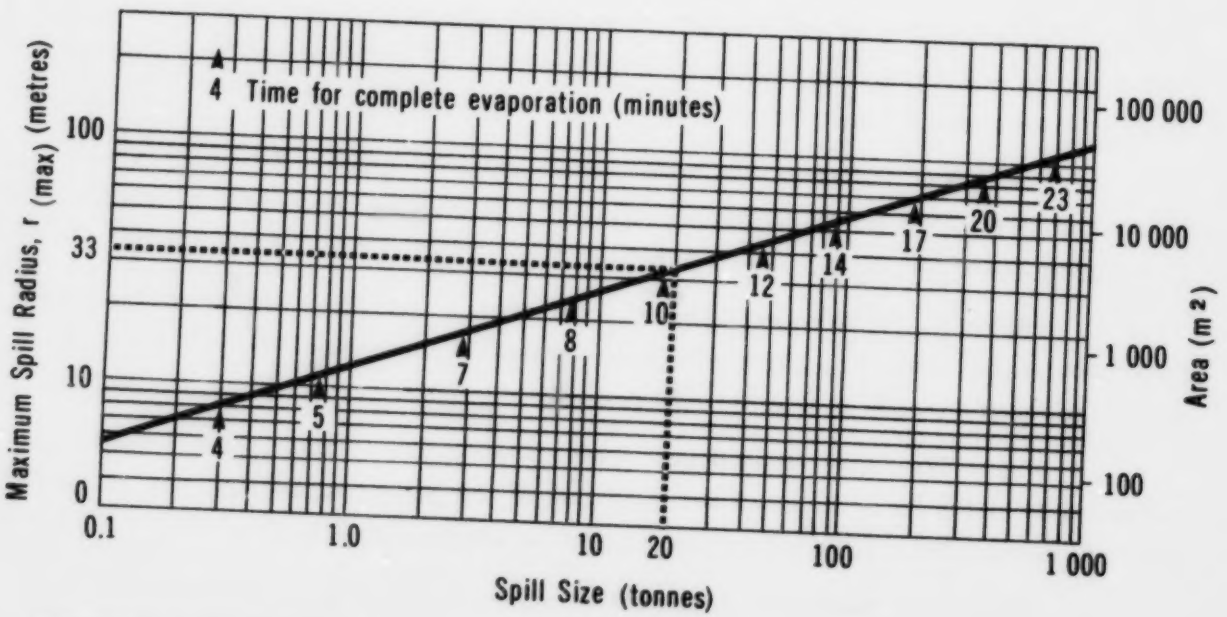
Figure 30: average concentration versus volume for the hazard zone for a range of spill sizes

5.4.4.1 Nomogram for spreading on still water. Assuming no dissolution in water, Figure 21 provides a simple means of estimating the maximum spill radius for ethylene oxide, if the spill size is known. The nomogram is based on data presented in the Hazard Assessment Handbook (CHRIS 1974) and on a computer model for simultaneous spreading

FIGURE 21

ETHYLENE OXIDE

MAXIMUM SPILL RADIUS vs SPILL SIZE



* Alpha and delta are conversion factors only and are of no significance other than to facilitate calculation of downstream concentration.

and evaporation of a cryogenic liquid spilled on water (Raj 1974). The arrow points on the nomogram provide an estimate of time for complete evaporation of the spill. Because of the short times involved, the complete time history of the spread of the spill has not been considered. Similarly, the translation distance of the spill by wind or surface current is not applicable.

5.4.4.2 Nomograms for dissolution in water - non-tidal rivers. The flowchart in Figure 22 outlines the steps required to estimate the downstream concentration after a spill and identifies the nomograms to be used. These nomograms (Figures 23 through 30) are described in the following subsections.

Figure 23: Time versus distance. Figure 23 presents a simple relationship between average stream velocity, time, and distance. Using an estimate of average stream velocity (U), the time (t) to reach any point of interest at some distance (X) downstream of the spill can be readily obtained from Figure 23.

Figure 24: Channel width versus hydraulic radius. The model used to estimate downstream pollutant concentrations is based on an idealized rectangular channel of width (W) and depth (d). The hydraulic radius (r) for the channel is required in order to estimate the turbulent diffusion coefficient (E). The hydraulic radius (r) is defined as the stream cross-sectional area (A) divided by the wetted perimeter (P). Figure 24 is a nomogram for computation of the hydraulic radius (r) using the width and depth of the idealized river cross-section.

Figure 25: Diffusion coefficient versus hydraulic radius. Figure 25 permits calculation of the longitudinal diffusion coefficient (E), knowing the hydraulic radius (r) from Figure 24 and the average stream velocity (U).

Figure 26: Alpha versus diffusion coefficient. Figure 26 is used to estimate a conversion factor, alpha (α), which is a function of the diffusion coefficient (E) and the time (t) to reach the point of interest downstream of the spill.

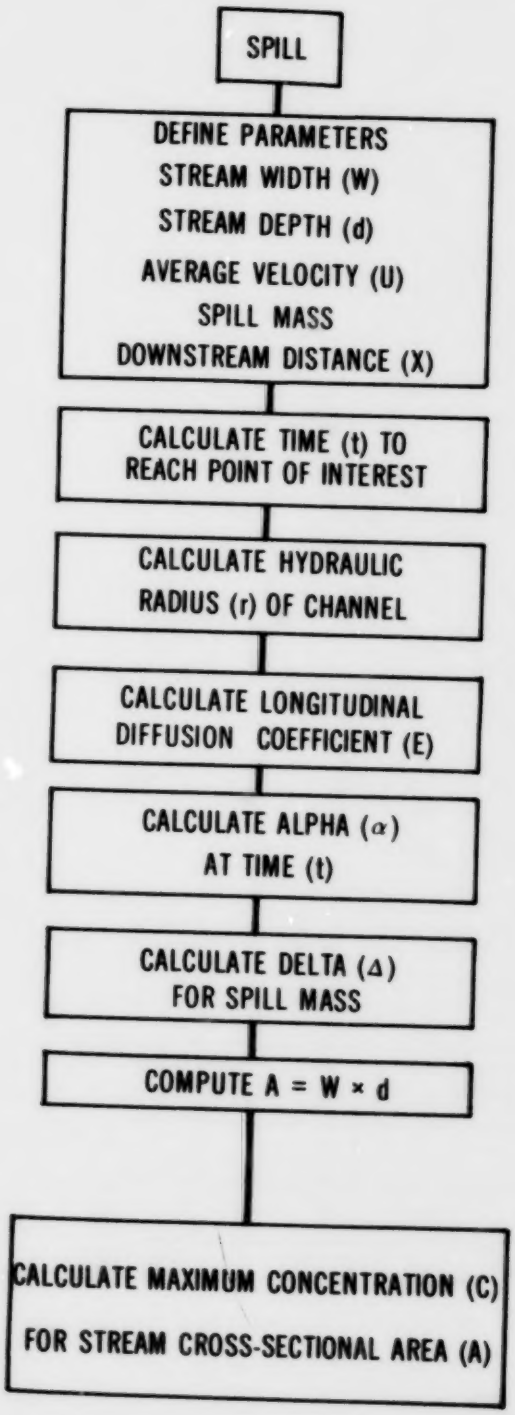
Figure 27: Alpha versus delta. A second conversion factor, delta (Δ), must be estimated from Figure 27 to allow determination of the pollutant concentration at the point of interest. Delta (Δ) is a function of alpha (α) and the spill size.

Figure 28: Maximum concentration versus delta. Figure 28 represents the final step for calculation of the maximum downstream pollutant concentration (C) at the point of interest. Using the factor delta (Δ) and knowing the stream cross-sectional area (A), the concentration (C) is readily obtained from the nomogram. The value

FIGURE 22

ETHYLENE OXIDE

FLOW CHART TO DETERMINE POLLUTANT CONCENTRATION IN NON-TIDAL RIVERS


SPILL
DEFINE PARAMETERS
STREAM WIDTH (W)
STREAM DEPTH (d)
AVERAGE VELOCITY (U)
SPILL MASS
DOWNSTREAM DISTANCE (X)
CALCULATE TIME (t) TO REACH POINT OF INTEREST
CALCULATE HYDRAULIC RADIUS (r) OF CHANNEL
CALCULATE LONGITUDINAL DIFFUSION COEFFICIENT (E)
CALCULATE ALPHA (α) AT TIME (t)
CALCULATE DELTA (Δ) FOR SPILL MASS
COMPUTE A = W × d
CALCULATE MAXIMUM CONCENTRATION (C) FOR STREAM CROSS-SECTIONAL AREA (A)

Step 1: Observed or Estimated

W = _____ m

d = _____ m

U = _____ m/s

MASS = _____ tonnes

X = _____ m

Step 2: Use Figure 23

t = _____ minutes

Step 3: Use Figure 24

r = _____ m

Step 4: Use Figure 25

E = _____ m^2/s

Step 5: Use Figure 26

α = _____

Step 6: Use Figure 27

Δ = _____

Step 7: Compute stream cross-sectional Area (A)

A = W × d _____ m^2

Step 8: Use Figure 28

C = _____ ppm

FIGURE 23

ETHYLENE OXIDE

TIME vs DISTANCE

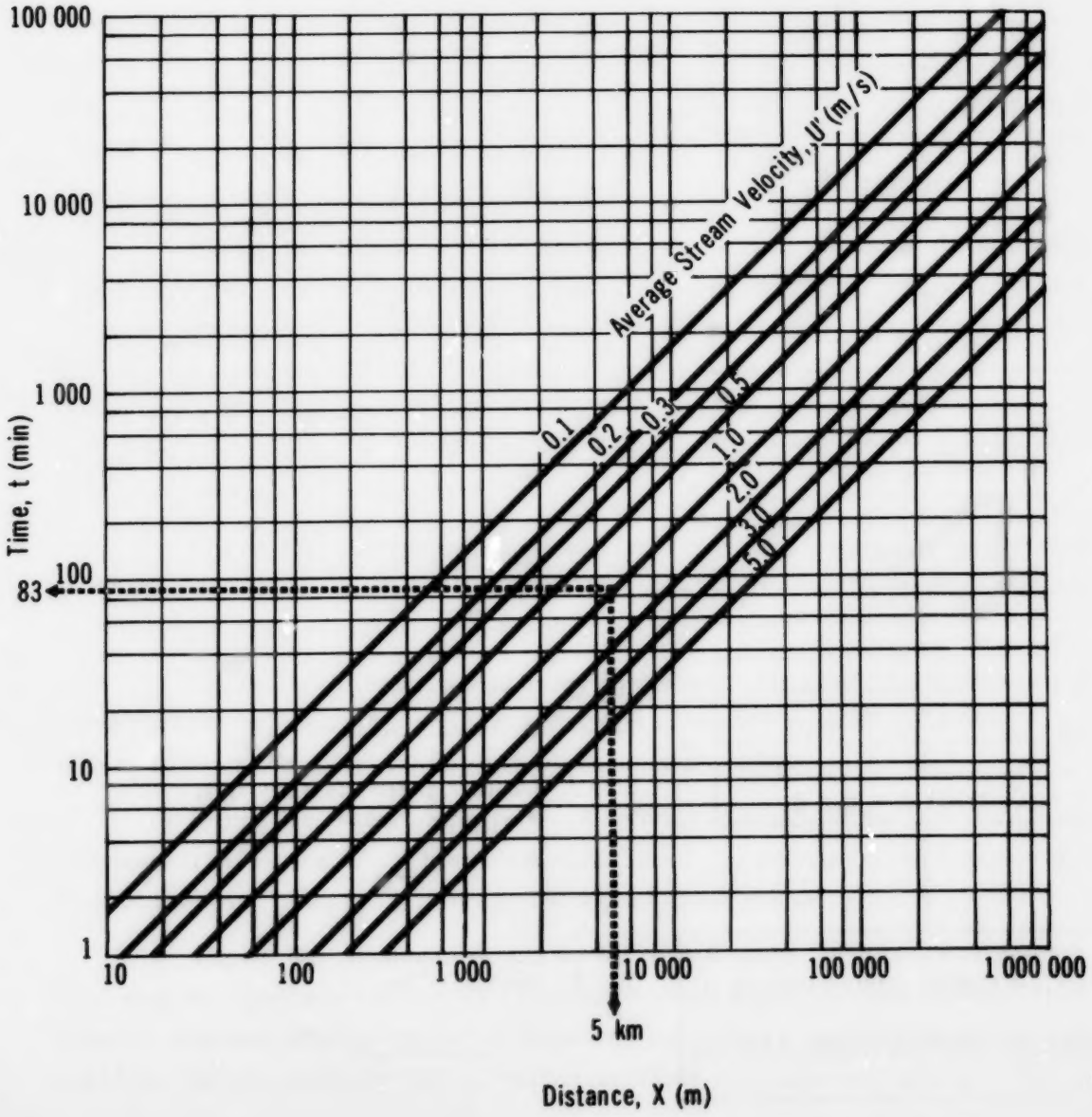


FIGURE 24

ETHYLENE OXIDE

CHANNEL WIDTH VS HYDRAULIC RADIUS

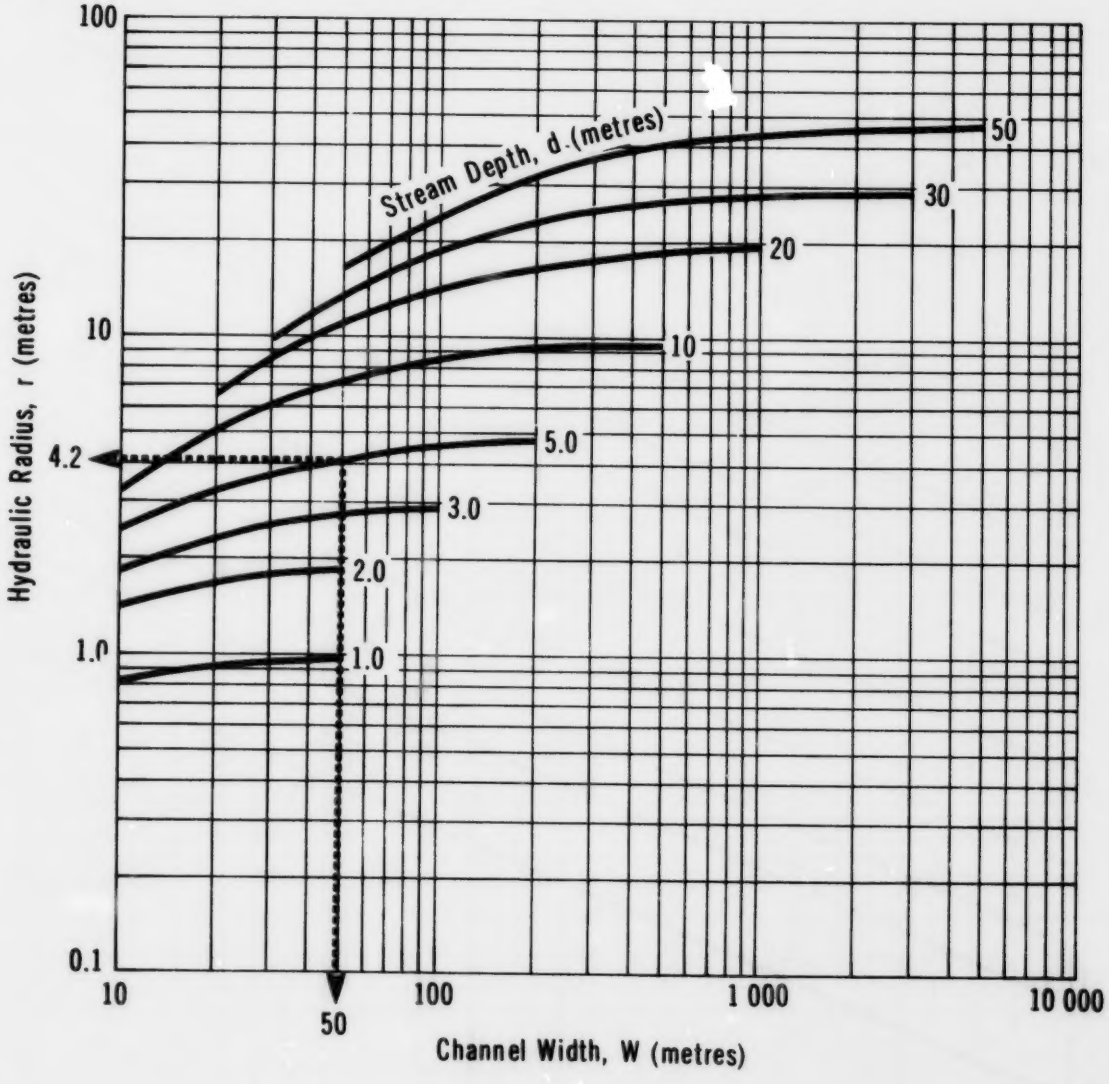


FIGURE 25

ETHYLENE OXIDE

DIFFUSION COEFFICIENT VS HYDRAULIC RADIUS

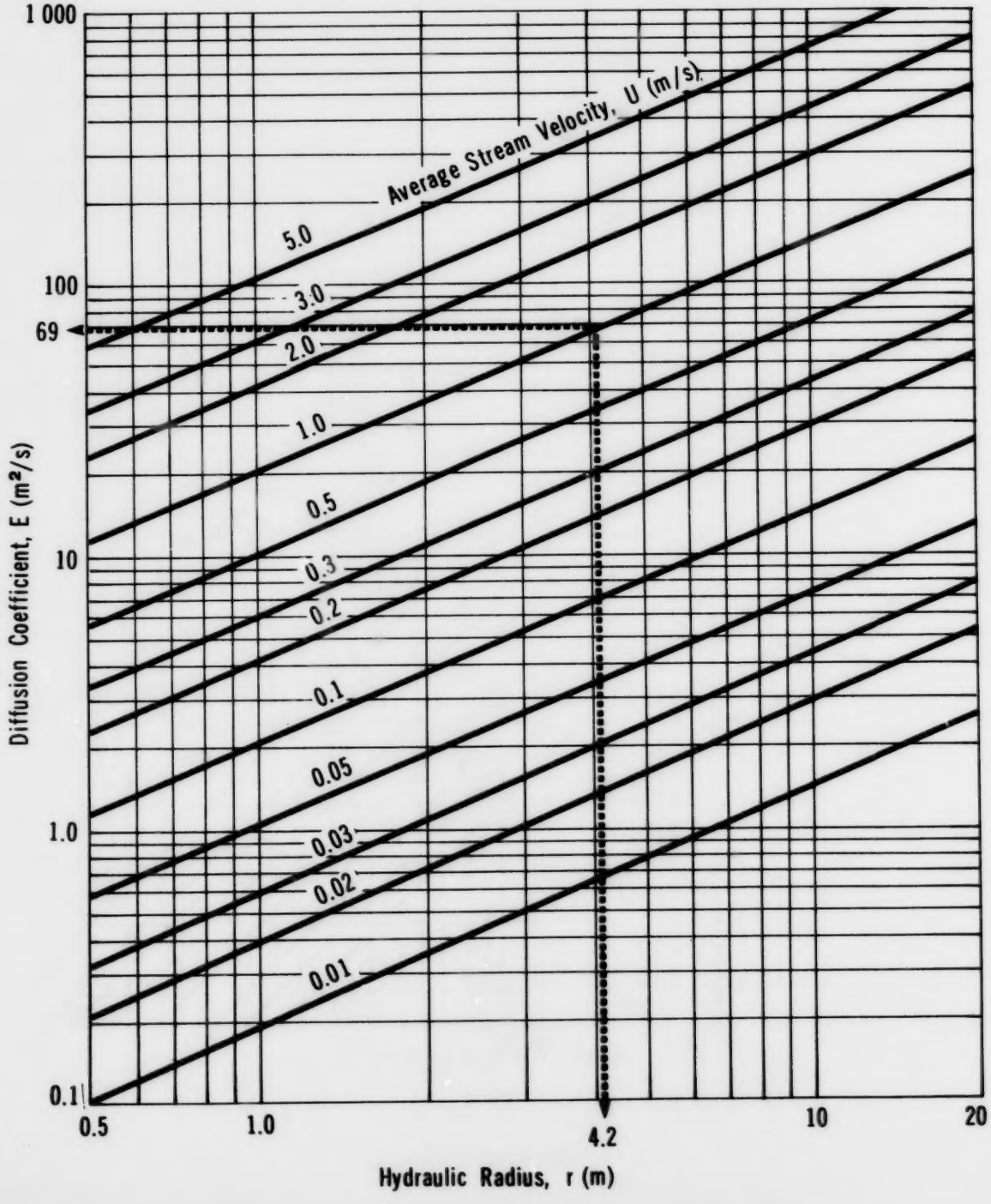


FIGURE 26

ETHYLENE OXIDE

ALPHA vs DIFFUSION COEFFICIENT

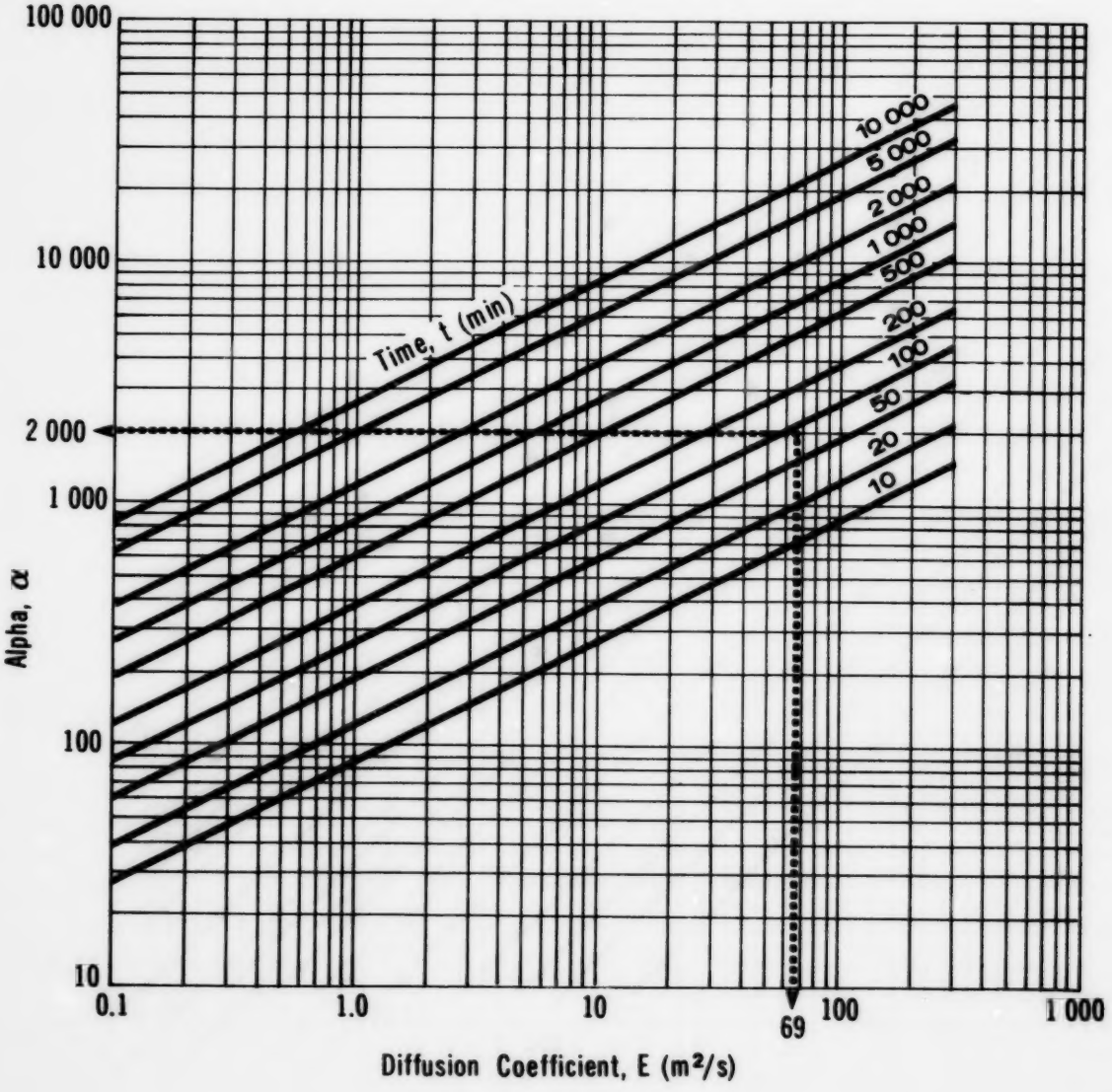


FIGURE 27

ETHYLENE OXIDE

ALPHA vs DELTA

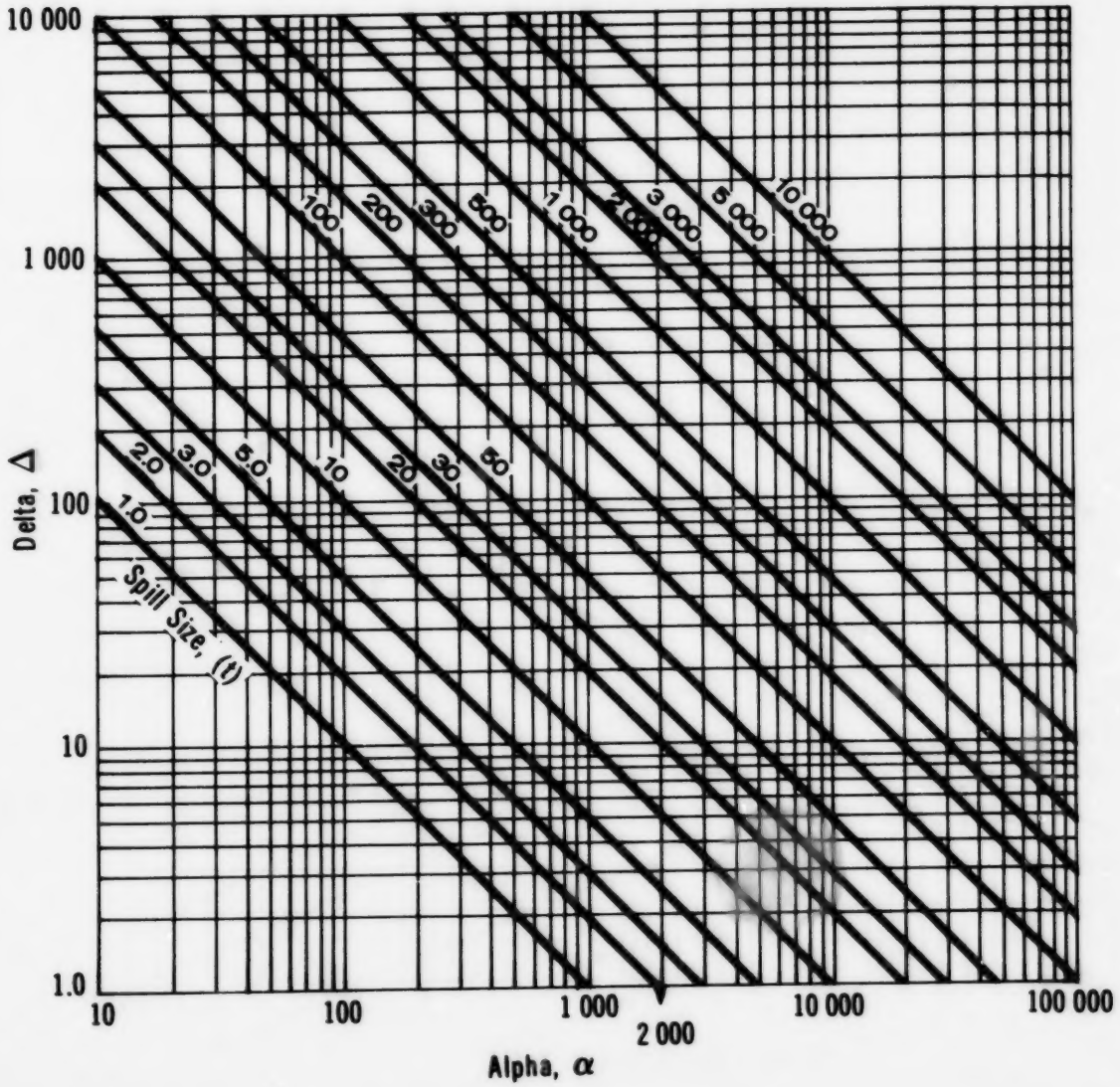
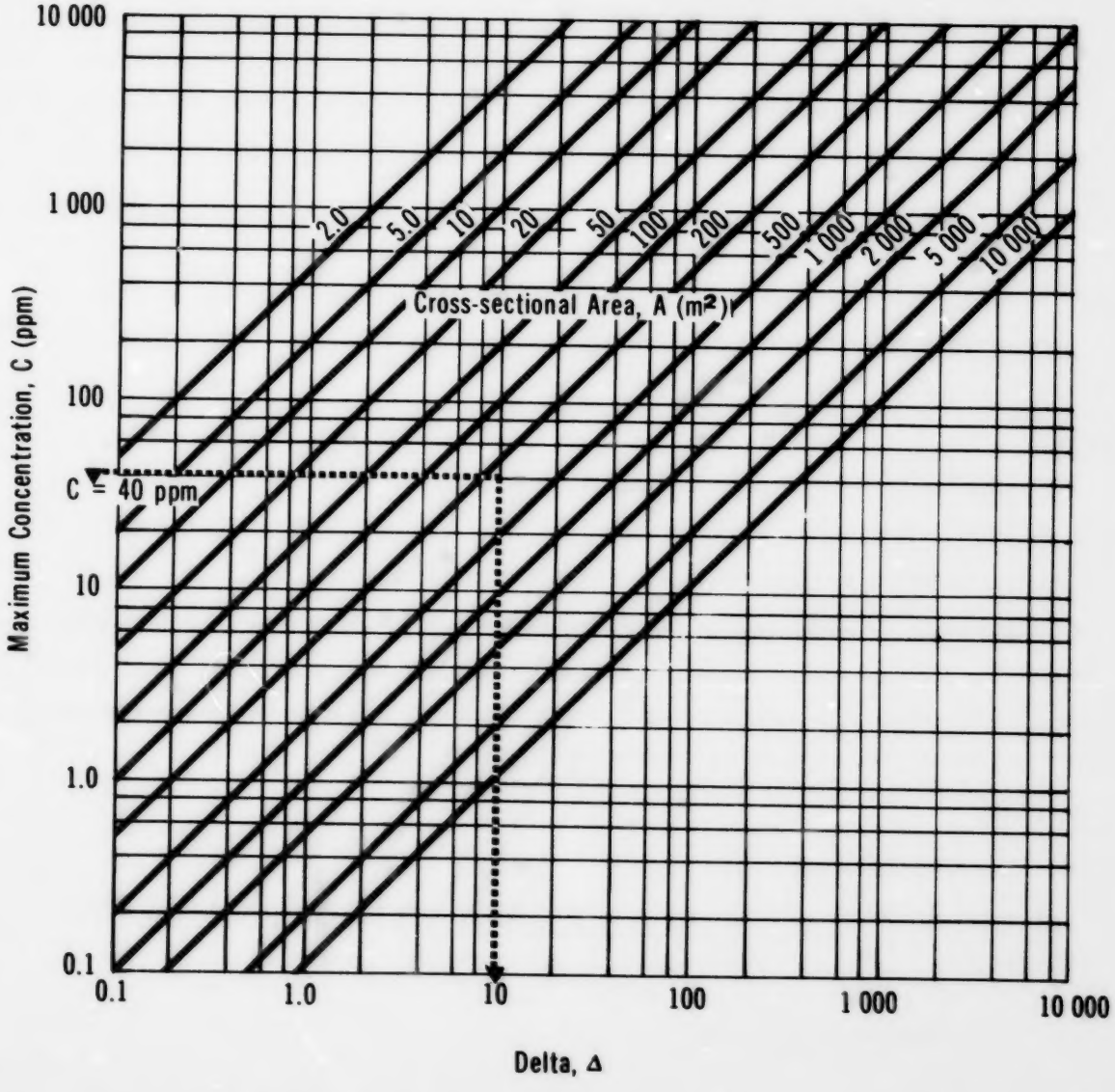


FIGURE 28

ETHYLENE OXIDE

MAXIMUM CONCENTRATION vs DELTA



obtained from Figure 28 applies to neutrally buoyant liquids or solids and will vary somewhat for other pollutants which are heavier or lighter than water.

5.4.4.3 Nomograms for lakes or still water bodies.

Figure 29: Volume versus radius. The spill of a neutrally buoyant liquid in a lake in the absence of wind and current has been idealized as a cylinder of radius (r) and length (d), equivalent to the depth of the lake at the point of spill. The volume of water in the cylinder can be obtained from Figure 29. The radius (r) represents the distance from the spill to the point of interest.

Figure 30: Average concentration versus volume. For a known volume of water (within the idealized cylinder of radius (r) and length (d)), the average concentration of pollutant (C) can be obtained from Figure 30 for a known mass of spill. This assumes the pollutant is spread evenly throughout the cylinder. For pollutants that are more or less dense than water, the actual concentration at the bottom would be higher or lower, respectively.

5.4.5 Sample Calculations.

5.4.5.1 Spread on still water. A 20 tonne spill of ethylene oxide has occurred on a large lake. What is the maximum size of the spill (assuming no dissolution) and approximate time for complete evaporation?

Solution

- Use Figure 21
- With spill size = 20 tonne, r_{max} = 33 m
- Time for complete evaporation is a little over 10 minutes

5.4.5.2 Pollutant concentration in non-tidal rivers. A 20 tonne spill of ethylene oxide has occurred in a river. The stream width is 50 m and the stream depth is 5 m. The average stream velocity is estimated at 1 m/s. What is the maximum concentration expected at a water intake located 5 km downstream?

Solution

Step 1: Define parameters

- W = 50 m
- d = 5 m
- U = 1 m/s
- Spill size = 20 tonnes

FIGURE 29

ETHYLENE OXIDE

VOLUME VS RADIUS

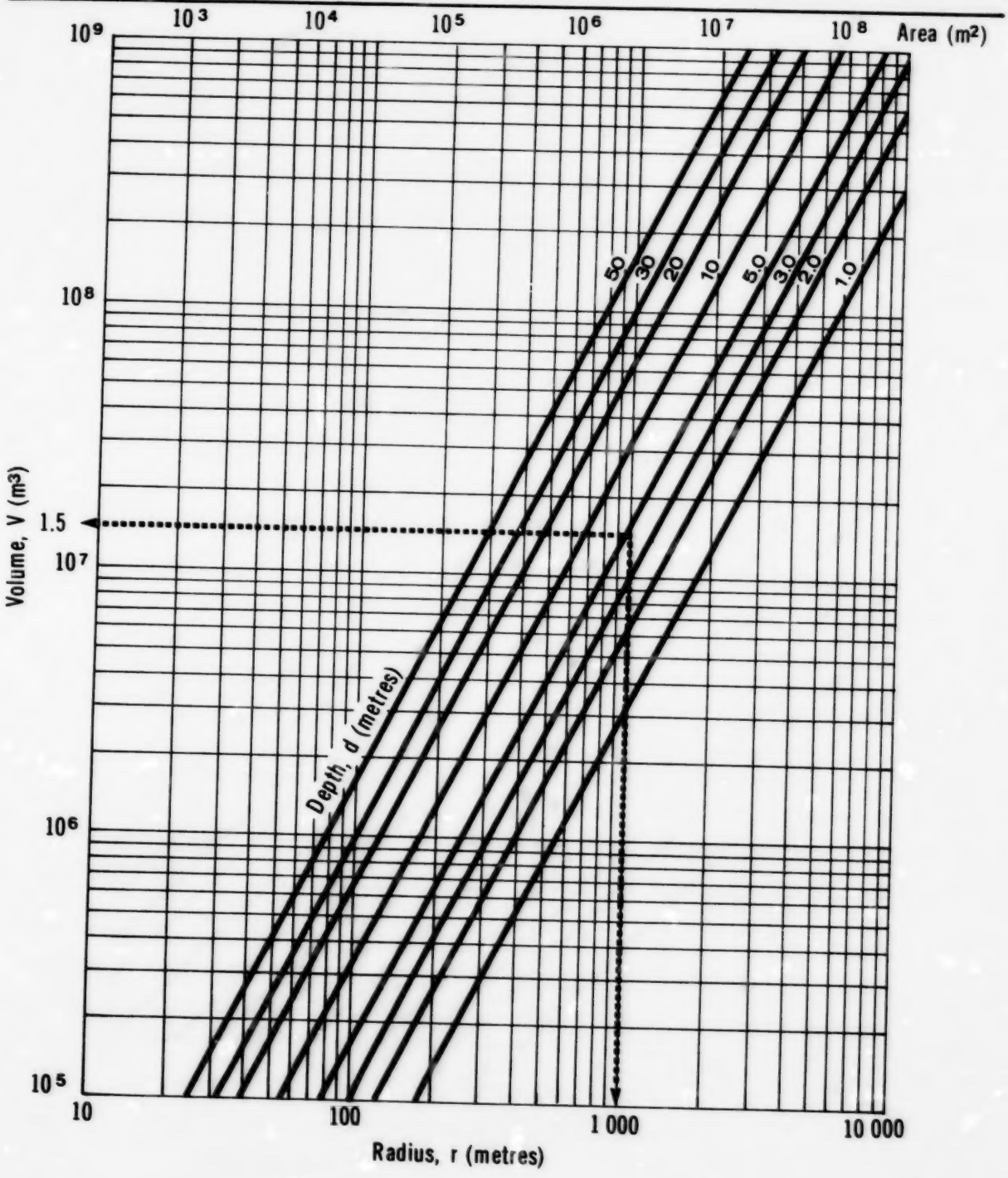
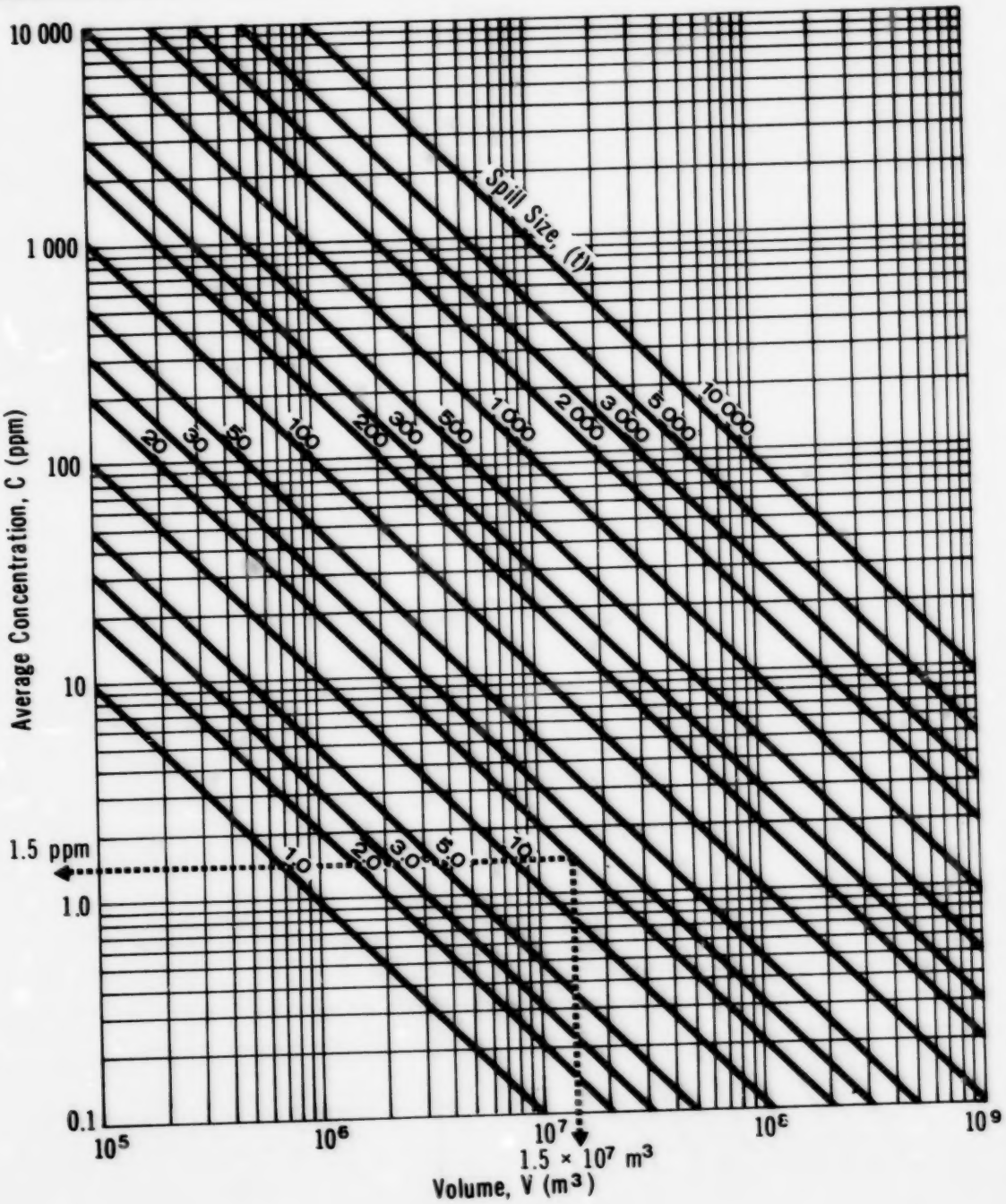


FIGURE 30

ETHYLENE OXIDE

AVERAGE CONCENTRATION vs VOLUME



Step 2: Calculate the time to reach the point of interest

- Use Figure 23
- With X = 5000 m and U = 1 m/s, t = 83 min

Step 3: Calculate the hydraulic radius (r)

- Use Figure 24
- With W = 50 m and d = 5 m, r = 4.2 m

Step 4: Calculate the longitudinal diffusion coefficient (E)

- Use Figure 25
- With r = 4.2 m and U = 1 m/s, E = 69 m^2/s

Step 5: Calculate alpha (α)

- Use Figure 26
- With E = 69 m^2/s and t = 83 min, α = 2000

Step 6: Calculate delta

- Use Figure 27
- With alpha (α) = 2000 and spill size = 20 tonnes, delta (Δ) = 10

Step 7: Compute the stream cross-sectional area (A)

- A = W x d = 50 x 5 = 250 m^2

Step 8: Calculate the maximum concentration (C) at the point of interest

- Use Figure 28
- With Δ = 10 and A = 250 m^2, C = 40 ppm

5.4.5.3 **Average pollutant concentration in lakes or still water bodies.** A 20 tonne spill of ethylene oxide has occurred in a lake. The point of interest is located on the shore approximately 1000 m from the spill. The average depth between the spill site and the point of interest is 5 m. What is the average concentration which could be expected?

Solution

Step 1: Define parameters

- d = 5 m
- r = 1000 m
- spill size = 20 tonnes

Step 2: Determine the volume of water available for dilution or

- Use Figure 29
- With r = 1000 m, d = 5 m, the volume is approximately 1.5 x 10^7 m^3

Step 3: Determine the average concentration

- Use Figure 30
- With V = 1.5 x 10^7 m^3 and spill size = 20 tonnes, the average concentration is 1.5 ppm

5.5 Subsurface Behaviour: Penetration into Soil

5.5.1 Mechanisms. The principles of contaminant transport in soil and their application to this work are presented in the Introduction Manual. Special considerations related to the spill of ethylene oxide onto soil and its transport downward through the soil are presented here.

After a spill of ethylene oxide, evaporation will occur. While most of the material will be lost to evaporation, the balance will infiltrate the soil. Evaporation will continue within the soil but at a reduced rate.

Since ethylene oxide is miscible with water, the presence of water in the soil or falling as precipitation at the time of the spill will influence the rate of chemical movement in the soil. Dilution through mixture with water will increase the viscosity more than the mass density. This will have the net effect of reducing the velocity of downward movement in the soil. This will also result in a decrease in the vapour pressure and reduce the rate of evaporation. If the soil surface is saturated with moisture at the time of the spill, as might be the case after a rainfall, the spilled chemical will run off or pond and eventually evaporate.

For this work, the soils have been assumed to be at field capacity. This situation provides very little interstitial water to dilute the chemical during transport or to impede its downward movement and thus represents "worst case" analysis.

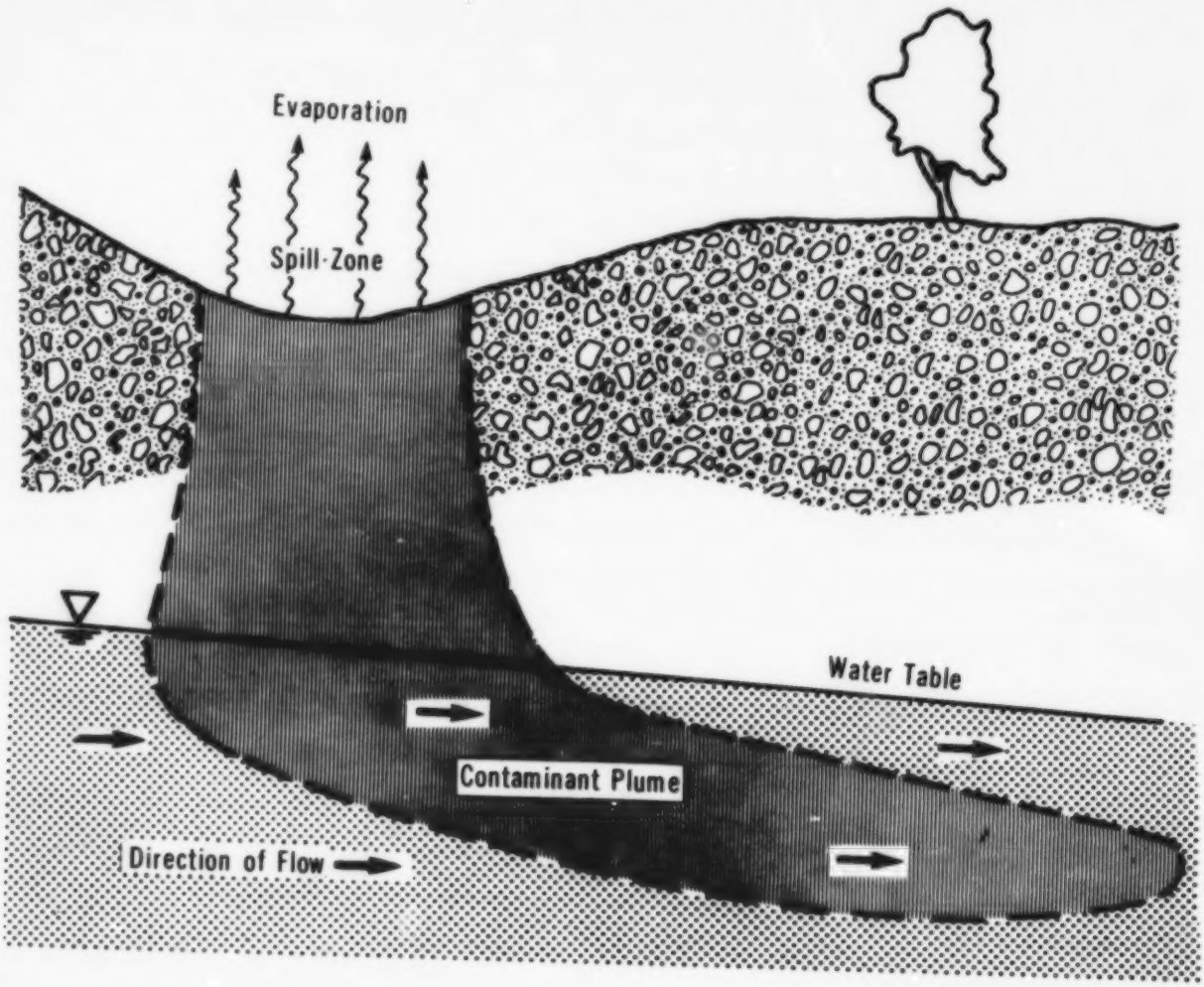
During transport downward, ethylene oxide may interact with the soil as well as evaporate. However, it is assumed that sufficient material will remain to allow movement toward the groundwater table. Upon reaching the groundwater table, the contaminant will continue to move, now in the direction of groundwater flow. A contaminated plume will be produced, with dilution and dispersion serving to reduce the concentration. This is shown schematically in Figure 31.

5.5.2 Equations Describing Ethylene Oxide Movement into Soil. The equations and assumptions used to describe contaminant movement downward through the unsaturated soil zone toward the groundwater table have been described in the Introduction Manual. Transport velocities have been based on Darcy's Law assuming saturated piston flow.

FIGURE 31

ETHYLENE OXIDE

SCHEMATIC SOIL TRANSPORT



Soil: Coarse Sand

–Porosity (n) = 0.35

–Intrinsic Permeability (k) = 10^{-9} m^2

–Field Capacity (θ_{fc}) = 0.075

5.5.3 Saturated Hydraulic Conductivity of Ethylene Oxide in Soil. The saturated hydraulic conductivity (K_o), in m/s, is given by:

$$K_o = \frac{(\rho g)k}{\mu}$$

where: k = intrinsic permeability of the soil (m^2)

ρ = mass density of the fluid (kg/m^3)

μ = absolute viscosity of the fluid (Pa·s)

g = acceleration due to gravity = 9.81 m/s^2

The fluids involved are ethylene oxide and water. The water calculations represent the extreme as ethylene oxide is diluted.

Property	Ethylene Oxide (4°C)	Water (20°C)
Mass density (ρ), kg/m^3	895	1000
Absolute viscosity (μ), Pa·s	0.29×10^{-3}	1.0×10^{-3}
Saturated hydraulic conductivity (K_o), m/s	$(3.03 \times 10^7)k$	$(0.98 \times 10^7)k$

5.5.4 Soils. Three soils were selected for this work. Their relevant properties are:

	Soil Type		
Property	Coarse Sand	Silty Sand	Clay Till
Porosity (n), m^3/m^3	0.35	0.45	0.55
Intrinsic permeability (k), m^2	10^{-9}	10^{-12}	10^{-15}
Field capacity (θ_{fc}), m^3/m^3	0.075	0.3	0.45

5.5.5 Penetration Nomograms. Nomograms for the penetration of ethylene oxide into the unsaturated zone above the groundwater table were prepared for the three soils listed above. They present penetration time (t_p) plotted against depth of penetration (B). Because of the methods and assumptions used, the penetration depth should be considered as a maximum depth, in time t_p.

A flowchart for the use of the nomograms is presented in Figure 32. The nomograms are presented as Figures 33, 34, and 35. The water lines on the nomograms represent the maximum penetration of water at 20°C in time t_p. It is a limiting condition as ethylene oxide becomes diluted with water.

5.5.6 **Sample Calculation.** A 40 tonne spill of ethylene oxide has occurred on silty sand. The temperature is 4°C; the spill radius is 8.6 m. Calculate the depth of penetration 2 days after the spill. Since data are not available to estimate the amount evaporated, assume that one-half evaporates before penetrating.

Solution

Step 1: Define parameters

- Mass spilled = 40 000 kg
- Amount remaining for penetration = amount spilled less amount evaporated = 40 000 kg - 20 000 kg = 20 000 kg
- T = 4°C
- r = 8.6 m
- Soil = silty sand
- Groundwater table depth (d) = 13 m
- Time since spill (t_p) = 2 d

Step 2: Calculate the area of the spill

- $A = \pi r^2 = 232\ m^2$

Step 3: Estimate the depth of penetration (B) at time (t_p)

- For silty sand, B = 5 m at t_p = 2 d
- Groundwater table has not been reached in this time

FIGURE 32

ETHYLENE OXIDE

FLOWCHART FOR NOMOGRAM USE

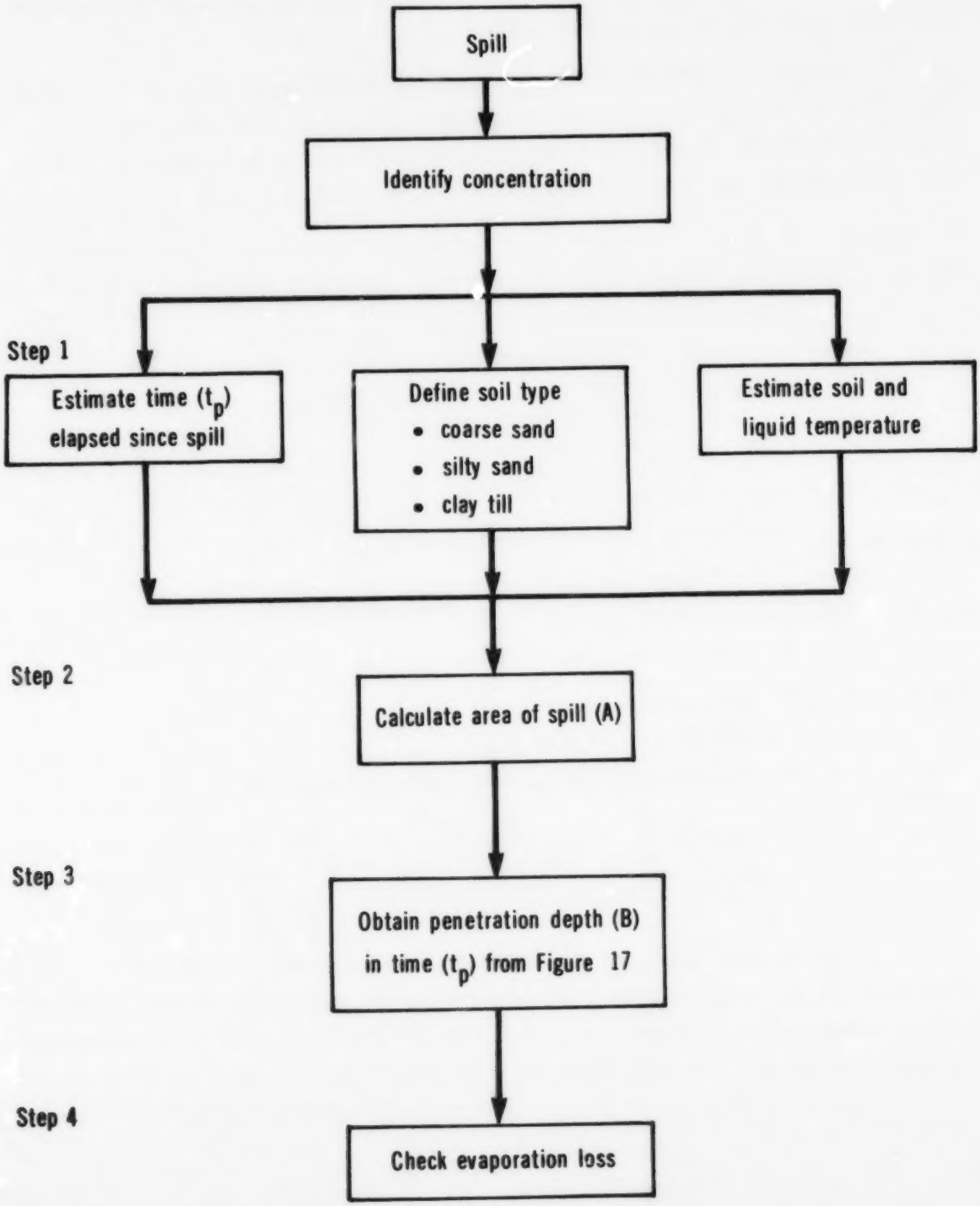


FIGURE 33

ETHYLENE OXIDE

PENETRATION IN COARSE SAND

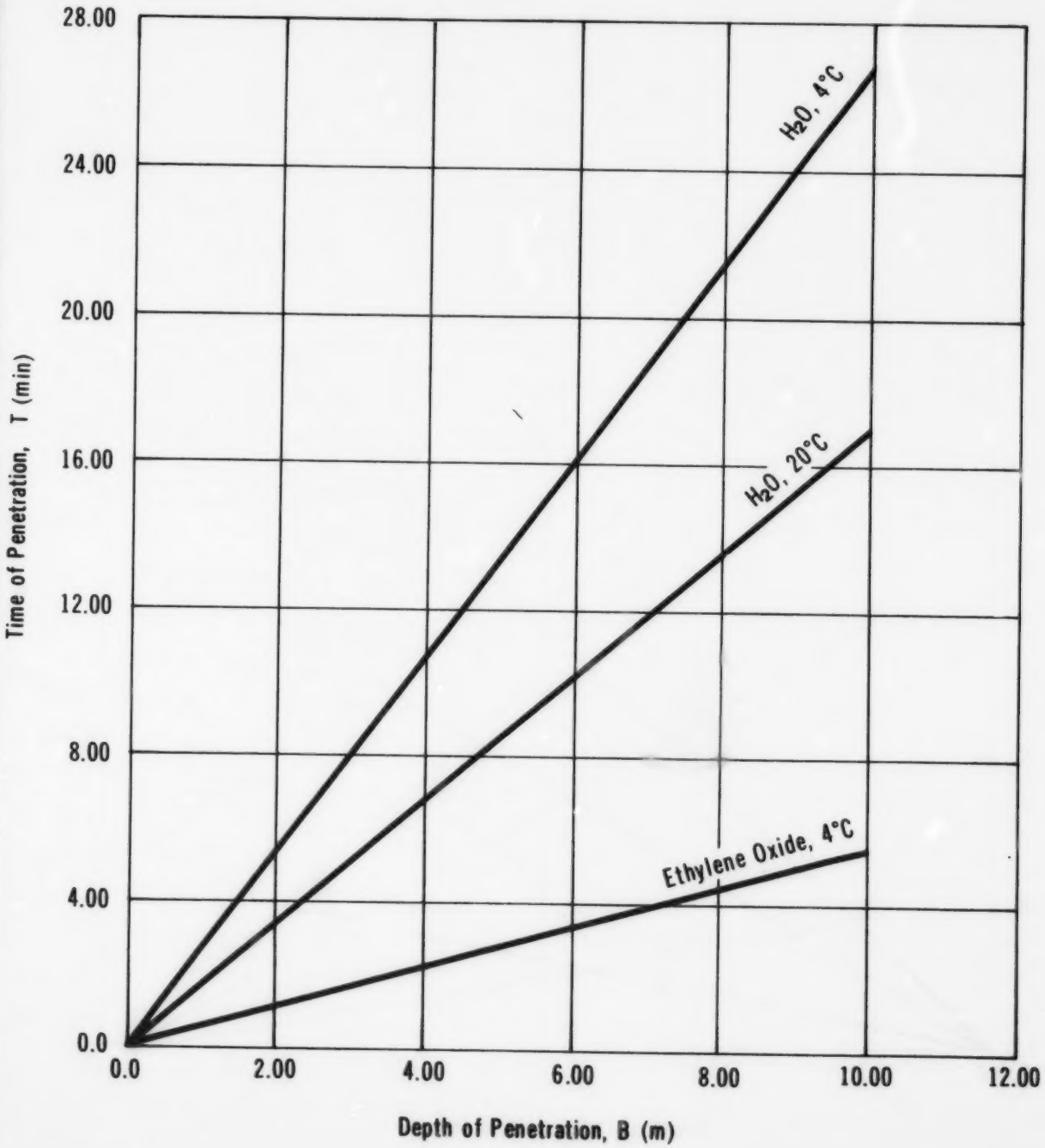


FIGURE 34

ETHYLENE OXIDE

PENETRATION IN SILTY SAND

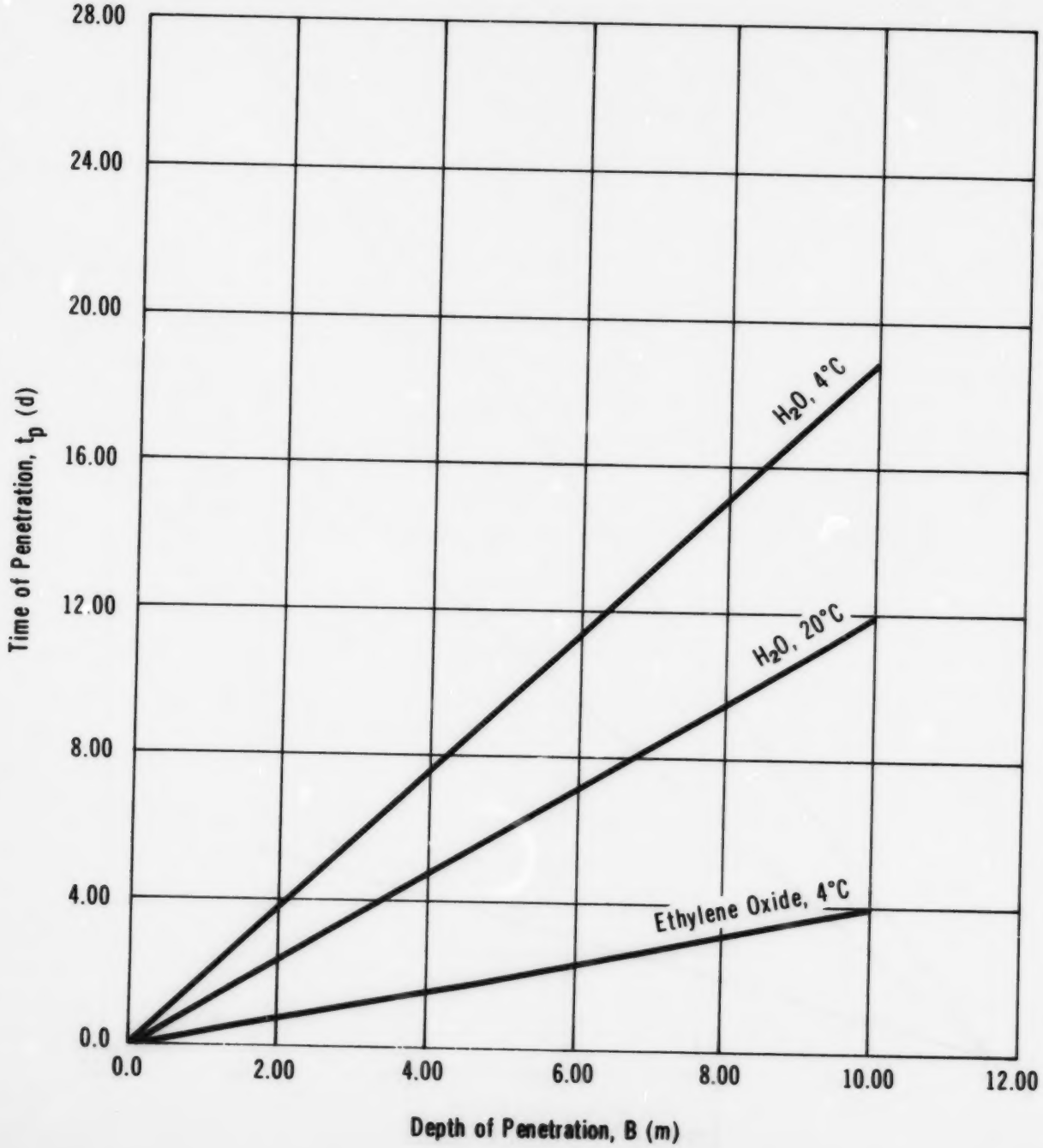
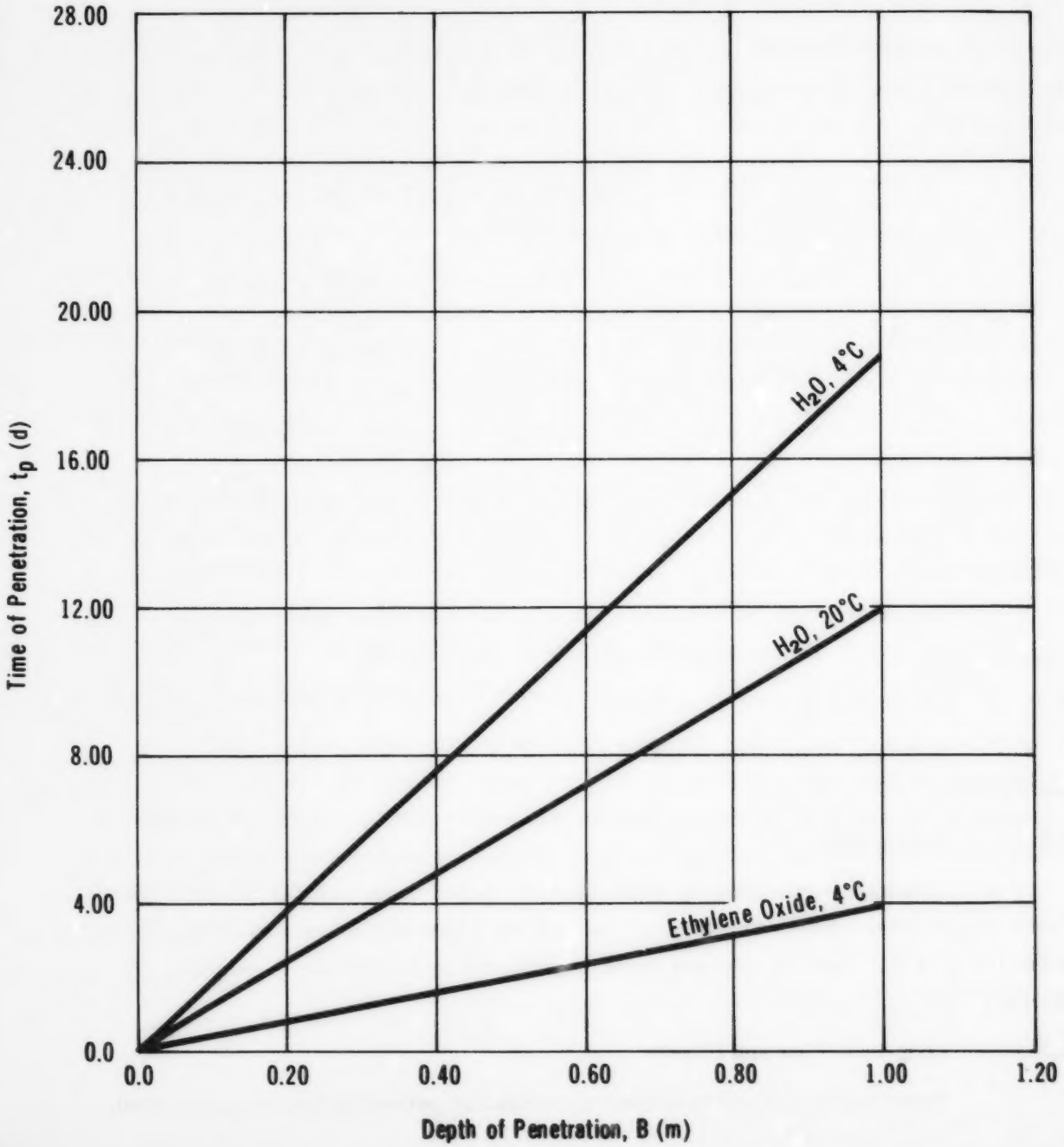


FIGURE 35

ETHYLENE OXIDE

PENETRATION IN CLAY TILL



6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water. Canada has no regulated limits for ethylene oxide in water.

6.1.2 Air. Ontario's airborne limit is 28 500 $\mu g/m^3$ (Ontario E.P. Act, 1971).

6.2 Aquatic Toxicity

6.2.1 U.S. Toxicity Rating. Ethylene oxide has been assigned a TL_m96 of 10 to 100 ppm (RTECS 1979).

6.2.2 Measured Toxicities. No fish kill data were available.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Fish Toxicity Tests					
90	24	Goldfish	TL_m	ASTM D1345	Verschueren 1984
90	24	Goldfish	LC_{50}	Aerated, pH 7.8, 20°C	Bridié 1979

Microorganisms

Ethylene oxide is commonly used as a sterilizing agent because of its bactericidal activity. The material is very toxic to microorganisms.

6.3 Other Land and Air Toxicities

Ethylene oxide affects germination of seeds and shows mutagenic effects in plants (OHM-TADS 1981).

6.4 Degradation

Ethylene oxide has a BOD of 0.06 (w/w) and a COD of 1.74 (w/w) (Verschueren 1984). Ethylene oxide has half-life in water of 76 hours at 37°C, and of 6 months at 4°C. Loss of ethylene oxide is primarily by conversion to ethylene glycol (EOPD 1977).

6.5 Long-term Fate and Effects

Bioconcentration and food chain accumulation potentials have not been cited.

7 HUMAN HEALTH

The toxic effects of ethylene oxide for man and animals have been well documented in several review documents (NIOSH 1977b, 1981; Patty 1981). A large amount of data report skin and eye irritation, as well as systemic effects due to ethylene oxide exposure. In addition, mutagenic effects in at least 13 biological species have been reported. Evidence of carcinogenesis has been reported in rats (NIOSH 1981). In human studies, there has been some evidence of increased chromosomal aberrations in exposed male workers; two epidemiological studies have reported cancers among exposed workers. There is also some evidence from animal studies weakly supporting a conclusion of teratogenic potential due to exposure to ethylene oxide.

On the basis of both the human and animal data reported since 1977, NIOSH issued Current Intelligence Bulletin No. 35 in 1981 recommending that ethylene oxide be regarded in the workplace as a potential occupational carcinogen. On January 8, 1982, Health and Welfare Canada issued a hospital alert warning of the potential health effects of exposure to ethylene oxide. A Canada Safety Council Hazard Warning was published in April of the same year.

The toxicological data summarized here have been extracted from reliable standard reference sources. It should be noted that some of the data are for chronic (long-term), low-level exposures and may not be directly applicable to spill situations. With the exception of data pertaining to mutagenicity, teratogenicity and carcinogenicity, only acute (short-term) exposure data are given for nonhuman mammalian species, to support interpretation of the human data where appropriate.

7.1 Recommended Exposure Limits

The exposure standards for ethylene oxide are based upon its potential effects as a primary irritant and sensitizing agent, although both the USA-ACGIH and NIOSH recommend a reduction of the exposure standards in view of data indicating ethylene oxide's potential carcinogenic, mutagenic and reproductive effects (Doc. TLV 1981; NIOSH 1981). Canadian provincial guidelines generally are similar to those of the USA-ACGIH, unless indicated otherwise.

Guideline (Time)	Origin	Recommended Level	Reference
Time-weighted Averages (TWA)			
TLV• (8 h)*	USA-ACGIH	1 ppm (2 mg/m^3)	TLV 1983
Short-term Exposure Limits (STEL)			
No STEL limits are listed here as former levels of up to 75 ppm have been dropped because of the carcinogenic and mutagenatic effects found since promulgation of this level.			
Other Human Toxicities			
IDLH	USA-NIOSH	800 ppm	NIOSH Guide 1978
TC_{LO}	-	12 500 ppm (10 s)	RTECS 1979
LC_{50}	-	4000 ppm (4 h)	AAR 1981

* Note: In recent times, the TLV• has fallen from 50 ppm (as recent as 1979) to 10 to 5 to 1 ppm. Many other agencies are following this movement and thus other guidelines will be listed here.

Inhalation Toxicity Index

The Inhalation Toxicity Index (ITI) is a measure of the potential of a substance to cause injury by inhalation. It is calculated as follows:

ITI = 1315.12 (Vapour Pressure, in mm Hg/TLV•, in ppm)

At 10°C, ITI = 1315.12 (758 mm Hg/10 ppm)

At 10°C, ITI = 9.9×10^4

7.2 Irritation Data

7.2.1 Skin Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
1 to 100 percent (18 s to 60 min)	Various applications in aqueous solution resulted in 3/8 of test subjects showing a positive response, one at 20 days and two at 19 days.	Patty 1981

Exposure Level (and Duration)	Effects	Reference
1 percent	A single challenge to workers with an average exposure of 10.4 years produced no observable sensitization in the 30 workers.	Patty 1981
1 percent (7 s)	Irritation.	RTECS 1979
Unspecified	Contact with even dilute solutions may cause irritation, blistering, edema and necrosis of the skin.	Patty 1981

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
"Dilute solutions"	May cause irritation and necrosis.	Patty 1981
Liquid	Severe burns.	Matheson 1980
SPECIES: Rabbit		
18 mg (6 h)	Moderate irritation.	RTECS 1979
0.5 mg/dose (20 min intervals for 6 h, 5 d)	Minimal conjunctival congestion.	Alcon 1973. IN NIOSH 1977b
1 to 20 percent	Irritant effects observed after acute ocular installation were: discharge, iritis, corneal cloudiness and damage as evidenced by fluorescein staining. Conjunctival congestion and flare were seen after administration to the anterior chamber.	McDonald et al. 1973. IN NIOSH 1977b
2.1 percent in aqueous solution	Initiation of irritation.	Glaser 1979

7.3 Threshold Perception Properties

7.3.1 Odour.

Odour Characteristics: Sweet, ether-like, oleofinic (Verschueren 1984).

Odour Index: 2000 (Verschueren 1984).

Parameter	Media	Concentration	Reference
Odour Recognition Threshold	in air	500 ppm	ASTM 1980
Odour Detection Threshold	in air	250 ppm	ASTM 1980
Mean Detectable Concentration	in air	700 ppm	Fed. Reg. 1982
Absolute Perception Limit	in air	260 ppm	Verschueren 1984

7.3.2 Taste. No data.

7.4 Toxicity Studies

7.4.1 Inhalation.

Exposure Level (and Duration)	Effects	Reference
Acute Exposure		
SPECIES: Human		
12 500 ppm (10 s)	TC_{LO}, Irritation.	RTECS 1979
4000 ppm (4 h)	LC_{50}	AAR 1981
500 ppm (2 min)	Nausea, vomiting, changes in respiration.	DRES 1980
Unspecified	Diarrhea, headache, vomiting, confusion, excitement, reversible neurological changes.	Patty 1981
SPECIES: Dog		
1300 to 1400 ppm (4 h)	3/3 test animals died on first day.	Glaser 1979
960 ppm (4 h)	LC_{50}	RTECS 1979

Exposure Level (and Duration)	Effects	Reference
SPECIES: Cat		
2200 ppm (3 h)	Death within 24 hours.	Patty 1981
2200 ppm (1 1/2 h)	Injurious, no death.	Patty 1981
SPECIES: Guinea Pig		
51 000 to 64 000 ppm (10 min)	Death in 24 hours.	Patty 1981
51 000 to 64 000 ppm (5 min)	Majority died within 1 to 8 days.	Patty 1981
14 000 ppm (20 min)	Majority died within 1 to 8 days.	Patty 1981
14 000 ppm (10 min)	No evidence of injury.	Patty 1981
7000 ppm (150 min)	LD_{LO}	TDB (on-line) 1981
7000 ppm (1 h)	Death of majority within 1 to 8 hours.	Patty 1981
7000 ppm (1/3 h)	No evidence of injury.	Patty 1981
3000 ppm (3 h)	Death of majority within 1 to 8 hours.	Patty 1981
3000 ppm (1 h)	No deaths.	Patty 1981
2200 ppm (4 h)	Injurious, few deaths.	Patty 1981
1300 to 1400 ppm (8 h)	Majority died within 1 to 8 days.	Patty 1981
1100 ppm (8 h)	Slight injury, no death.	Patty 1981
560 to 600 ppm (8 h)	Occasional death.	Patty 1981
250 to 280 ppm (8 h)	Slight respiratory changes, no deaths.	Patty 1981
SPECIES: Rat		
1462 ppm (4 h)	LC_{50}	RTECS 1979
1100 ppm (8 h)	Death within 24 hours.	Patty 1981
SPECIES: Mouse		
836 ppm (4 h)	LC_{50}	AAR 1981

Exposure Level (and Duration)	Effects	Reference
Chronic Exposures		
SPECIES: Human		
5 to 10 ppm (10 yr)	No evidence of ill effects noted in 37 chemical operators who worked in ethylene oxide production for over 10 years.	Doc. TLV 1981
Unspecified (1 yr)	Three sterilizer users in hospital were hospitalized with lower limb neuropathy. Effects were reversible.	Patty 1981

7.4.2 Ingestion.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Guinea Pig		
270 mg/kg	LD_{50}	RTECS 1979
SPECIES: Rat		
242 to 282 mg/kg (in aqueous solution)	LD_{50}	Glaser 1979
170 mg/kg	LD_{50}	Glaser 1979
72 mg/kg	LD_{50}	RTECS 1979
SPECIES: Dog		
Various	The biological half-life was found to be 32 minutes. The major metabolite is ethylene glycol.	Darby 1978

7.4.3 Mutagenicity, Teratogenicity and Carcinogenicity.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
<50 ppm (2.9 yr) (average)	Statistically significant increase in numbers of chromosomal aberrations in peripheral lymphocytes obtained from blood of exposed workers. There was also a statistically significant increase in numbers of sister chromatid exchanges in peripheral lymphocytes of some workers exposed to ethylene oxide. Data from sperm analysis were inconclusive.	Abrahams 1980. IN NIOSH 1981
20 ± 10 ppm	Mixed exposure to methyl formate and ethylene oxide. In a 5 year period, 3 cases of leukemia occured (expected: 0.2).	Hogstedt et al. 1979. IN NIOSH 1981
0.6 to 14 ppm with excursions to 730 ppm	Historical prospective mortality study in Swedish ethylene oxide manufacturing facility. Employees were exposed for more than 1 year. Nine cancer deaths were observed, compared with 3.4 expected; leukemia, stomach cancer and circulatory disease related deaths were all higher than expected.	Hogstedt et al. 1979. IN NIOSH 1981
Unspecified	Cohort study among full-time exposed workers, intermittently exposed workers and controls. The full-time exposed cohort showed a considerable excess of mortality derived mainly from increased mortality from tumours and diseases of the circulatory system and showed a significant excess of cancer incidence.	Hogstedt et al. 1979. IN NIOSH 1981
Unspecified: peaks less than 50 ppm	Cohort study among full-time workers exposed to ethylene oxide showed increases in breaks and exchanges in cells during a cytogenetic test.	Abrahams 1980

Exposure Level (and Duration)	Effects	Reference
SPECIES: Rat		
10, 33 and 100 ppm (12 wk, 5 d/wk prior to mating; 7 d/wk during and after mating)	Significant reduction in the number of pups born per litter in the group of highest exposure. Fewer pregnancies.	Union Carbide 1979. IN NIOSH 1981
10, 33 and 100 ppm (6 h/d, 5 d/wk, 2 yr)	Incidences of mononuclear cell leukemia and peritoneal mesothelioma were significantly increased. Among female rats, a linear dose-response relationship was established at 10 ppm and 33 ppm exposures.	Snellings et al. 1981 IN NIOSH 1981
10, 33 and 100 ppm (6 h/d, 5 d/wk; 6, 12, 18 or 24 mo)	Incidence of leukemia was higher for all groups, especially for higher exposures and longer exposure times.	Fed. Reg. 1982
1000 ppm (4 h)	Male rats exposed; progeny showed higher death rates - indicating male sperm adversely affected.	Fed. Reg. 1982
SPECIES: Mouse		
1000 ppm (4 h)	Dominant lethal mutations.	Embree et al. 1977. IN NIOSH 1981
600 to 800 ppm	Reported dose-response relationship for unschedule DNA synthesis (UDS) in the testes of mice.	Cumming et al. 1981. IN NIOSH 1981
0, 75 and 150 mg/kg (1 d during some portion of gestation)	Significant reduction in mean fetal body weight, in numbers of malformed fetuses. High incidence of maternal mortality at high dosages during some other portions of the gestation period.	La Borde et al. 1980. IN NIOSH 1981
150 mg/kg	Investigators reported dominant lethal mutations following intraperitoneal administration of a single dose of ethylene oxide.	Generoso et al. 1980. IN NIOSH 1981
0.1, 0.3 and 1.0 mg (91 wk)	Subcutaneous administration to female mice. Sarcomas appeared at the injection site beginning the 50th week.	Dunkelberg 1979. IN NIOSH 1981

Exposure Level (and Duration)	Effects	Reference
30 to 60 mg/kg (1 d)	Male mice were exposed intraperitoneally. Mice mated and male progeny were studied for sperm translocation heterozygosity. A dose-response relationship was observed. 38/406 of animals had HT in the high dose group and 6/456 in the low dose group.	Generoso et al. 1980. IN NIOSH 1981
SPECIES: Other		
Various	Ethylene oxide has been shown effective as both an alkylating agent and a mutagen in viruses, *Salmonella typhimurium*, *Escherischia coli*, *Neurospora crassa*, barley, rice, wheat and *Tradecantia paludosa*.	NIOSH 1981; Holliday 1982
Various	Studies in *Drosophila melanogaster* exposed to ethylene oxide have revealed an increase in both sex-linked recessive lethal, and autosomal deletion mutations in a dose-response relationship. Lethal mutations and translocations have been induced in all stages of spermatogenesis.	NIOSH 1981

7.5 Symptoms of Exposure

General symptoms of exposure found in most information sources have not been specifically referenced. Only those of a more specific or unusual nature have their sources indicated.

7.5.1 Inhalation.

1. Irritation of the mucous membranes and respiratory system (DRES 1982).
2. Headache.
3. Drowsiness.
4. Numbing of the sense of smell.
5. Delayed nausea (AAR 1981).

6. Vomiting.
7. General anesthetic effect.
8. Emphysema.
9. Bronchitis.
10. Lymphocytosis.
11. Dyspnea.
12. Edema of the lungs.
13. CNS depression.

7.5.2 Ingestion.

1. Symptoms very similar to those of inhalation.

7.5.3 Skin Contact.

1. Irritation.
2. Dermatitis.
3. Frostbite.
4. Blisters.
5. Burns.

7.5.4 Eye Contact.

1. Irritation.
2. Lacrimation.
3. Burns.

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Ethylene Oxide with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
GENERAL														
Fire		•	•										Although soluble in water, solutions will continue to burn until diluted to 22 volumes of water to one of ethylene oxide.	Sax 1979; NFPA 1978
Heat		•	•	•			•						Flammable liquid; vapours form explosive mixtures with air; exothermic polymerization may occur in vessel.	Sax 1979; NFPA 1978; Bretherick 1979
SPECIFIC CHEMICALS														
Acetylene		•											Produces explosive acetylides.	Bretherick 1979
Aluminum Chloride	•		•											NFPA 1978
Aluminum Oxide	•		•											NFPA 1978
Ammonia		•	•											Bretherick 1979
Ammonium Hydroxide		•												Leleu 1976

8.1 Compatibility of Ethylene Oxide with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Magnesium Perchlorate		•												NFPA 1978
m-Nitroaniline		•											Explosion in autoclave at 150°C.	Bretherick 1979
Potassium	•			•										NFPA 1978
Propylene Oxide	•	•			•			•		•			Rapid exothermic reaction @ 300°C.	Bretherick 1979
Trimethylamine		•											Reaction may be delayed.	Bretherick 1979
CHEMICAL GROUPS														
Acids	•			•										NFPA 1978
Alcohols		•												Bretherick 1979
Alkali Metal Hydroxides	•			•										NFPA 1978
Alkanethiols		•												Bretherick 1979
Bases				•										NFPA 1978
Explosives		•												EPA 600/2-80-076
Iron Chlorides	•			•										NFPA 1978
Iron Oxides	•			•										NFPA 1978

8.1 Compatibility of Ethylene Oxide with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Mercaptans			•											NFPA 1978
Oxidizing Agents	•	•											Possible evolution of toxic fumes.	EPA 600/2-80-076
Reducing Agents	•												May produce flammable hydrogen gas.	EPA 600/2-80-076
Tin Chlorides	•			•										NFPA 1978
Water Reactives	•		•			•							Explosion may also occur or highly unstable mixtures may result.	EPA 600/2-80-076

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

The following procedures have been derived from a literature review. To avoid any deviation from the intended meaning, the wording of the original source has been presented essentially unchanged - in so doing, it is recognized that there may be discrepancies between different sources of information. It is recognized that countermeasures are dependent on the situation, and thus what may appear to be conflicting information may in fact be correct for different situations. The following procedures should not be considered as Environment Canada's recommendations.

9.1.1 Fire Concerns. Ethylene oxide is an extremely flammable liquid (Dow ERIS 1981). The vapours form explosive mixtures with air and may travel along surfaces to distant ignition sources and flash back (NFPA 1978).

It can undergo hazardous, exothermic, polymerization (explosion hazards). In the presence of catalysts such as pure iron, aluminum oxides and alkali metal hydroxides or the anhydrous chlorides of iron, aluminum or tin, ethylene oxide can undergo highly exothermic molecular rearrangement and/or self-polymerization (GE 1980).

If the liquid fire is extinguished, a reflash or explosion hazard remains because ethylene oxide is a liquefied gas and will continue to generate explosive vapour-air mixtures (MCA 1971). Fires involving large quantities of liquid ethylene oxide are difficult to extinguish. Fire may continue until dilution with at least 22 parts of water. Removal of oxygen, i.e., smothering, may also be ineffective as ethylene oxide will continue to burn even in low oxygen situations.

9.1.2 Fire Extinguishing Agents. Use water spray at a safe distance to cool containers involved in a fire to prevent rupture. Water spray will not put out fire until water dilution of ethylene oxide is at least 22:1, up to at least 100:1 (NFPA 1978; GE 1980; CCPA 1983).

Small fires: Dry chemical, CO_2, water spray or (alcohol) foam.
Large fires: Water spray, fog or foam.

Stay away from ends of tanks. For massive fire in cargo area, use unmanned hose holder or monitor nozzles (ERG 1980; GE 1980).

9.1.3 Evacuation. The following information consists of evacuation distances which appear in the literature. Important parameters such as spill quantity, concentration level

to which evacuation is suggested, and environmental conditions, may not be defined. Readers are advised to evaluate the use of these values with those derived from the methods to calculate hazard zones in Section 5.3 of this manual, which uses the above data.

The following are recommended evacuation distances from the immediate danger area of a spill, based on prevailing winds of 10 to 19 km/h (EAG 1978):

Approximate Size of Spill (m^2)	Distance to Evacuate from Immediate Danger Area	For Maximum Safety, Downwind Evacuation Area Should be (m)
20	25 m (30 paces)	160 long, 160 wide
35	30 m (36 paces)	160 long, 160 wide
55	35 m (48 paces)	320 long, 160 wide
75	40 m (54 paces)	320 long, 160 wide

In the event of an explosion, the minimum safe distance from flying fragments is 600 m in all directions.

9.1.4 Spill Actions, Cleanup and Treatment.

9.1.4.1 General. Stop or reduce discharge of material if this can be done without risk. Eliminate all sources of ignition. Avoid skin contact and inhalation (Celanese MSDS 1979). Leaking containers should be removed to the outdoors or to an isolated, well-ventilated area and the contents transferred to other suitable containers (MCA 1971).

9.1.4.2 Spills on land. Contain if possible by forming mechanical and/or chemical barriers to prevent spreading (EPA 670/2-75-042). Hycar may be used to reduce vapour emissions and to absorb liquid.

9.1.4.3 Spills in water. Contain if possible and apply activated carbon at 10 percent the spill amount over the region occupied by 10 mg/L or greater concentrations. Use mechanical dredges or lifts to remove the carbon (EPA 670/2-75-042)

9.1.5 Disposal. Waste ethylene oxide must never be discharged directly into sewers or surface waters. It may be burned in an approved incinerator.

9.1.6 Protective Measures. For entry into a situation where the spilled material and its characteristics are unknown, self-contained breathing apparatus and a totally encapsulated chemical suit should be worn.

If the spilled material is known to be ethylene oxide:

- Chemical safety goggles, impervious clothing and self-contained breathing apparatus should be worn (Celanese MSDS 1979).
- The following clothing material shows breakthrough times of about 1 hour: butyl rubber, nitrile, and chlorinated polyethylene. The following show breakthrough times of much less than 1 hour: natural rubber, neoprene, PVC and Viton (Little 1983).
- Do not use protective clothing that has come into contact with ethylene oxide (GE, 1980). Leather clothing should not be reworn but should be disposed of by immersing in water for several days and then land-filling. Rubber clothing may be aerated for a number of days before reuse (CCPA 1983).
- Eyewash stations, safety showers and washing facilities should be readily available in areas of use and spill situations (GE 1980).
- A full facepiece is required above 500 ppm (GE 1980).
- Approved self-contained or supplied air respirators should be available for emergency and nonroutine exposures above the TLV (GE 1980).

9.1.7 Storage Precautions.

9.1.7.1 General. Store in a cool (<30°C), well-ventilated, isolated area (preferably separated, outside) which is low in fire-risk and protected with a well-designed sprinkler system. Keep away from sources of heat and ignition. Keep inside storage at a minimum. Large tanks require diking. Protect containers from physical damage. Ground all lines and equipment to protect from static sparks. Storage should have positive pressure inerting with nitrogen. Use explosion-proof electrical services (GE 1980). Ethylene oxide may undergo slow polymerization during storage. Safe storage pressures under nitrogen or methane blankets are recommended to be 150 kPa (10°C), 200 kPa (20°C) and 350 kPa (30°C). Excessive temperatures or contamination with such impurities as water, alkalis, acids, metal oxides, iron salts, or aluminum salts could cause rapid polymerization (Kirk-Othmer 1980).

9.1.7.2 Drum storage. It is suggested that a 15 m separation between facilities be maintained. Drums should have a roof for protection from sunlight, precipitation, etc., and preferably be open-sided. When this is not possible, the area should be vented to achieve at least 12 air changes per hour. Since ethylene oxide is explosive, electrical requirements are Class 1, Group B, Division II. Empty drums are as dangerous as full ones and should be filled with nitrogen as soon as possible. Spark-proof tools should be available at storage and use sites (Bridge 1980).

10 PREVIOUS SPILL EXPERIENCE

10.1 General

This section contains information on previous spill experience which will be useful to readers in understanding spill response and countermeasures. Only those which meet the criteria are included, and thus the number of experiences is not an indication of the problems or frequency of spillage. As technology in spill control advances, this section will be updated in future manual revisions to include the most useful information.

10.2 Tank Car Spill (HMIR 1981)

A coupling device of a freight car which collided with a tank car carrying 98 500 L of ethylene oxide pierced the front of the tank car, causing the ethylene oxide to escape and ignite. Evacuation of an area within a radius of 0.8 km of the accident was undertaken. Air and land traffic was rerouted to prevent any danger from the ongoing fire. Fire fighters arrived at the spill site and applied water streams to cool the tank and minimize the risk of explosion. The ethylene oxide spilling from the puncture was allowed to burn off. Response crews arrived at the site and began to pump nitrogen into the top of the damaged tank. Nitrogen was introduced to increase the pressure on the ethylene oxide, forcing it to spill out of the tank and burn off at a faster rate, and to prevent a vapour buildup which could result in an explosion. The fire burned throughout the day and night.

On the next day, it was estimated that approximately 49 000 L of the product remained in the tank. Response crews then connected a 120 m pipe to the tank car and allowed the ethylene oxide to flow out the pipe at approximately 2 L/s and burn under control in a containment ditch. When the material had nearly all burned off and there was no longer a risk of explosion, fire fighters directed the water streams into the tank car and extinguished the fire.

11 ANALYTICAL METHODS

The general approach adopted for each of the Priority Chemicals was as follows.

Methods have been documented here for the analysis of samples from air, water and soil in a normally equipped chemical laboratory remote from the spill site. Customary sources of standard or recommended analytical methods were consulted, and outlines are presented for each chemical. These sources included publications of the U.S. National Institute for Occupational Safety and Health (NIOSH), the U.S. Environmental Protection Agency (EPA), the American Water Works Association (AWWA), the American Society for Testing and Materials (ASTM), and the American National Standards Institute (ANSI).

If the standard or recommended methods were judged to be reliable and specific enough for the analysis of environmental and materials samples from spill sites and if they do not require highly specialized laboratory equipment, no additional methods were sought.

If especially simple, reliable tests (e.g., commonly used industrial methods) were found, they have been presented as well.

11.1 Quantitative Method for the Detection of Ethylene Oxide in Air

11.1.1 Gas Chromatography (NIOSH 1977a). A range of 41 to 176 mg/m^3 (22.8 to 97.7 ppm) of ethylene oxide in air may be determined by gas chromatography using flame ionization detection.

A known volume of air is drawn through a series of two 10 cm x 8 mm O.D. glass tubes each containing 20/40 mesh activated charcoal. The front tube contains 400 mg whereas the backup tube contains 200 mg. Each tube has a plug of silylated glass wool at both ends. A sample size of 5 L of air at a flow rate of 50 mL/min is recommended. Samples should be analyzed rapidly or stored at low temperature if immediate analysis is not possible.

The charcoal tube sample is scored with a file and broken. The charcoal is transferred to a 5 mL Teflon stoppered sample container containing 2.0 mL of carbon disulphide. The same operation is performed on the backup section.

The samples should be allowed to desorb for 30 min. A 5 µL aliquot of sample is injected into a gas chromatograph equipped with a flame ionization detector. The

ethylene oxide is determined using a suitable electronic integrator to measure peak area in comparison with a standard curve.

Typical gas chromatograph conditions are: nitrogen carrier gas flow at 30 mL/min, hydrogen gas flow at 30 mL/min, air flow at 300 mL/min, injector temperature at 155°C, detector temperature at 200°C, column temperature at 150°C, and a 10 ft. by 1/8 in. stainless steel column packed with Porapak QS.

11.2 Qualitative Method for the Detection of Ethylene Oxide in Air

A range of 25 to 500 ppm (14 to 278 mg/m^3) of ethylene oxide in air may be determined with the use of a Drager gas detector tube for ethylene oxide. A known volume of air is drawn through a Drager gas detector tube for ethylene oxide using a Drager multi-gas detector pump. A colour change of the indicating layer from pale yellow to pale turquoise green indicates ethylene oxide (Drager 1979).

11.3 Quantitative Method for the Detection of Ethylene Oxide in Water

11.3.1 Partition Infrared (AWWA 1981). A range of 40 to 400 ppm of ethylene oxide in water may be determined using a partition infrared method which is suitable for a variety of organic compounds.

A minimum of 1 L of representative sample is collected in an appropriate container and acidified to pH 2 with dilute hydrochloric acid. A 5 mL volume of acid should be sufficient. The sample is transferred to a separatory funnel and a 30 mL volume of Freon® 113 (1,1,2-trichloro-1,2,2-trifluoroethane) is used to rinse the sample container and added to the separatory funnel. The solvent layer is drained into a 100 mL volumetric flask. Two more 30 mL Freon® extractions are carried out and the extracts combined in the 100 mL volumetric flask. The volume is adjusted to 100 mL with Freon®.

The sample is scanned on a suitable infrared spectrophotometer from 3200 to 2700 cm^{-1} using matched 1 cm cells. The sample concentration is determined from a calibration curve.

11.4 Qualitative Method for the Detection of Ethylene Oxide in Water

Ethylene oxide may be determined qualitatively in water by infrared spectrophotometry. The sample is collected as in Section 11.3.1 and extracted with Freon® 113 (1,1,2-trichloro-1,2,2-trifluoroethane).

The sample is scanned on a suitable double-beam recording infrared spectrophotometer from 3200 to 2700 cm^{-1} using matched 1 cm cells and Freon® in the

reference cell. The presence of a characteristic absorbance pattern indicates the presence of ethylene oxide (AWWA 1981).

11.5 Quantitative Method for the Detection of Ethylene Oxide in Soil

11.5.1 Partition Infrared (AWWA 1981). This method is used for the detection of concentrations greater than 40 ppm of ethylene oxide in soil.

Approximately 20 g of soil, accurately weighed, are collected in a glass jar. Freon® 113 (1,1,2-trichloro-1,2,2-trifluoroethane) is used to extract the ethylene oxide. Three extractions using 30 mL of Freon® each time are carried out. The extracts are combined in a 100 mL volumetric flask. The volume is adjusted to 100 mL with Freon®. The sample is scanned on a suitable infrared spectrophotometer from 3200 to 2700 cm^{-1} using matched 1 cm near infrared silica cells. The sample concentration is determined from a calibration curve.

11.6 Qualitative Method for the Detection of Ethylene Oxide in Soil

Ethylene oxide may be determined qualitatively in water by infrared spectrophotometry. The sample is collected as in Section 11.5.1 and extracted with Freon® 113 (1,1,2-trichloro-1,2,2-trifluoroethane).

The sample is scanned on a suitable double-beam recording infrared spectrophotometer from 3200 to 2700 cm^{-1} using matched 1 cm cells and Freon® in the reference cell. The presence of a characteristic absorbance pattern indicates the presence of ethylene oxide (AWWA 1981).

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